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ENGINEERING SERIES

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THE PRINCIPLES OF METALLURGY

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PREFACE

The author has long felt the definite need for a textbook of metallurgy covering ores and their treatment, the reduction and refining of common metals, refractories, fuels, and metallography. A knowledge of metallurgy is fast becoming of vital importance in the practice of engineering. Modern industry uses metals to such a great extent that every engineer should be familiar with the properties, methods of treatment, and limitations of the common metals. Electrical engineers could have accomplished but little without constant supplies of cheap and pure copper. Mechanical engineers would have achieved small success in the development of the modern automobile and airplane without alloy steels and aluminum. Without nickel steel our civil engineers would be unable to erect long-span bridges or our modern skyscrapers. The future will probably find industry even more dependent upon the metallurgist for new methods of treatment or new combinations of metals to meet the ever-increasing demands of our complex life. It is significant that many of our large manufacturing companies are finding it profitable to venture into the sacred precincts of pure science in examining the internal structure of the metallic atom in an endeavor to alter this arrangement so as to produce metals more suited to our needs. The present age is indeed the age of metals; and whether it is a tiny piece of some relatively rare metal for a radio tube or a huge ingot of alloy steel for a cracking still, such materials are absolutely essential to our present highly specialized industrial organization.

This volume represents an effort on the part of the author to present in a single textbook the subject of metallurgy, from the mining of the crude ore to the sale of the refined metal for use in industry. It is intended to present, in a clear, concise manner, only the basic principles involved, leaving the instructor to amplify the subject in question by lectures as his judgment dictates.

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THE PRINCIPLES OF METALLURGY

CHAPTER I

ORES AND METALS

ORES

1. Definition. An ore may be defined as a combination of minerals from which one or more metals can be recovered at a profit. Metallic iron may be extracted from many of our common rocks, but only the oxides of iron with at least 35 per cent of Fe are economically valuable. The presence of other metals than the one the metallurgist seeks to recover may interfere with the successful treatment of the ore. The physical condition of the ore, the location of the deposit, and its relation to a transportation system — all these are factors in determining whether or not a mineral aggregate may be called an ore. For example, a rock containing 25 per cent of Fe as Fe_2O_3 is not an ore of iron today; for although the iron can be extracted from such a rock, this iron cannot be sold at a profit in competition with that derived from rich ores containing from 50 to 60 per cent of Fe. The day is surely coming, however (if we continue to waste our natural resources), when an ore containing 25 per cent of Fe will be valuable.

The location of the mineral deposit often determines whether or not the mineral is an ore. For example, a rock containing 6 ounces of Ag per ton, near cheap transportation and power, could be worked at a profit, but a similar deposit in some inaccessible region, served only by mule-back transportation, would be valueless.

Improvements in the art of metallurgy naturally play their part in making a deposit valuable. Twenty-five years ago the lowest-grade copper ore being treated contained about 2.5 per cent of Cu. Today, owing to improvements in grinding, gravity concentration, and oil flotation, copper ores as low grade as 0.9 per cent of Cu are being worked at a profit. For years engineers knew of the existence of a mountain of low-grade copper ore in Bingham Canyon, Utah, but it was not until new methods

made possible cheap and efficient treatment that the deposit was worked. In 1926 the company working this deposit paid over $8,000,000 in dividends. Until the development of differential flotation a few years ago, many complex mixtures of the sulphides of Pb, Zn, Fe, and Cu were valueless despite the fact that they contained notable percentages of these valuable metals. Today an increasing proportion of our lead and zinc is being derived from such complex ores.

In general, ores are named from the dominant valuable metal. To use the same example, the ore of the Utah Copper Company contains (besides the *gangue*, or rock) iron, copper, sulphur, arsenic, antimony, silver, and gold. It is called a copper ore because that metal can be extracted at a profit and because the value of the copper far exceeds that of the silver or the gold.

2. Classification. From a metallurgical standpoint, ores can be divided into three classes, designated as follows: (1) native ores, (2) oxide ores, (3) sulphide ores.

Other terms which are used in describing ores and are frequently met with in metallurgy are *straight ores* or *simple ores*, *free-milling ores*, *complex ores*, and *refractory ores*.

Straight ores, or simple ores, are those which contain in the main only one kind of metal, such as copper, iron, gold, or silver.

Free-milling ores are those ores of gold or silver from which a considerable percentage of the metal can be extracted by the simple process of crushing and amalgamation; for example, the gold-quartz ores of California.

Complex ores are those which contain more than one kind of metal which can be profitably extracted. A very common ore in Colorado and Idaho is a mixture of *sphalerite* (ZnS) and *galena* (PbS). A considerable percentage of both these metals can be recovered by water concentration and oil flotation. They are usually designated by the combination of metals. For example, a galena ore containing 10 ounces of silver per ton would be known as a *lead-silver ore*.

Many combinations of metal are undesirable from a metallurgical standpoint. An ore may contain an appreciable per cent of valuable metal, and yet this may not be readily extracted, owing to the presence of some other element or elements that interfere with the process. In a certain district in Canada there

is a large deposit of sulphide ore containing about 6 per cent of copper and 10 per cent of zinc. Up to the present time no one has been found with courage enough to attempt the treatment of this ore on a commercial scale, although certain processes, on a laboratory scale, appear to promise success. To begin with, it is far removed from transportation, and a smelter would have to be erected near the mine. If, on the other hand, the ore were shipped out, a copper-smelter would purchase it (at a low price, owing to the zinc content) but would not pay for the contained zinc. On the other hand, a zinc-smelter would not buy it as a zinc ore, because of the low percentage of zinc and the high percentage of copper and iron. Some day new processes will be developed, so that the ore can be separated into two products, a zinc concentrate and a copper concentrate, and both metals won at a profit.

Refractory ores are those which are not amenable to the simple metallurgical processes. For example, certain gold ores containing small amounts of tellurium or large amounts of sulphur cannot be successfully treated by the cyanide process unless they are first roasted. Many smelting ores also require preliminary roasting or special treatment before they can be reduced in the blast furnace or converter.

3. Native ores. Because of the great affinity which most metals have for oxygen and sulphur, few of our valuable metals are found existing as such in nature. The most common occurring in the native state are silver, gold, copper, platinum, and mercury. Others have been found, but such occurrences are more in the nature of mineralogical curiosities. A large part of our copper formerly came from the mines of upper Michigan, where the native metal occurs in the conglomerate and *amygdaloidal* rocks. In the early days of mining in that district, masses of copper weighing up to 150 tons were taken out, but today these rich ores have been exhausted, and the companies are dependent upon low-grade ore averaging about 1 per cent Cu. It is worthy of note, in passing, that the copper obtained from these ores has certain desirable physical properties, so that it usually commands a premium on the market even over pure electrolytic copper. Native silver and gold are very common, and nearly all our platinum is derived from the placer deposits of Russia and Colombia, where it occurs as the native metal.

4. Oxide ores. This class includes the oxides, carbonates, and silicates of most of our common metals. There are some, like silver and gold, which are so resistant to the action of air and water that they do not readily form these compounds. Oxide ores form an important class metallurgically because of the ease with which they can be reduced and refined. Economically they are not so important, for they supply but a small percentage of our metals. They are formed by the decomposition and alteration of sulphide ores by means of percolating waters charged with oxygen and carbon dioxide. They are characteristic of the zone close to the surface of the earth, and for that reason most of these deposits have been located and long since worked out. The important ones in this class are those of copper, iron, lead, and zinc.

5. Sulphide ores. This is the largest and most important class of ores. Included in this, by common consent, are the selenides, tellurides, arsenides, and antimonides. Most of our common metals have an affinity for sulphur exceeded only by that for oxygen. As a result most of our nonferrous metals are derived from this class of ores. They are troublesome from a metallurgical standpoint, for it is a difficult and often complicated process to rid the refined metal of the last traces of some of these impurities.

6. Ore and gangue. *Gangue* is the term applied to that part of the mineral aggregate which has no economic value. Often it constitutes a large part of the mass, and its character may be such that it must be removed by some sort of preliminary treatment, such as water concentration or oil flotation, before the ore can be smelted. For example, a copper ore containing 2 per cent of Cu is a valuable one, but it contains so much gangue in the form of silica, carbonates, or rock-forming silicates that it must be crushed and concentrated before smelting. Smelting is a relatively expensive operation, and, generally speaking, it does not pay to smelt an ore containing less than 6 per cent of Cu. Sometimes the presence of considerable gold and silver may alter this condition.

7. High-grade and low-grade ores. These are terms met with frequently in the technical press. They refer more generally to the value than to the chemical composition of the ore. A high-grade gold ore (this may be modified by location) is one worth more than $50 per ton, a high-grade copper ore is one containing

more than 10 per cent of Cu, and a high-grade zinc ore is one containing at least 45 per cent of Zn.

8. Siliceous ores, calcareous ores, etc. The character of the gangue serves as a method of classifying ores as siliceous, argillaceous, calcareous, and ferruginous. Acid ores are those containing an excess of free silica (SiO_2), while basic ores are those containing little, if any, free silica.

9. Direct smelting versus concentration. While many of the ores today may be smelted just as they are taken from the earth, there is a large and ever-increasing proportion of these that must be concentrated, or increased in value by rejecting the gangue, before they can be reduced to the metal. The following table indicates the metallic content of ores which may be smelted direct and that of ores which should be concentrated, or milled:

	Direct Smelting	Concentration
Iron	40% Fe	25% Fe
Copper	6% Cu	0.9% Cu
Zinc	50% Zn	7% Zn
Lead	40% Pb	4% Pb
Tin	50% Sn	0.2% Sn (gravel) 4.0% Sn (lode)

It should be emphasized that actual practice may depart widely from these figures, owing to local conditions or to the characteristics of the ore. For example, there are only two companies concentrating material as low grade as 0.9 per cent of Cu, and most of our mills are operating on ore containing about 2.2 per cent of Cu. Again, while it may be economical to smelt directly an ore containing as little as 30 per cent of Pb, it might not be advisable, under certain other conditions, to smelt directly one containing as much as 40 per cent of Pb. Each ore constitutes a problem in itself, and the figures above are given only in an attempt to present the situation in a general way.

METALS

10. General. Metals form a group of elementary substances possessing characteristic properties of elasticity, strength, toughness, ductility, malleability, hardness, fusibility, high conductivity of heat and electricity, and resistance to atmospheric and

chemical action. Of the 55 metals classed as such by the chemist only about 25 occur in such quantity, or possess such valuable properties, as to render them of much consequence to the metallurgist. The metals commonly used in industry are

Aluminum	Iron	Silver
Antimony	Lead	Sodium
Bismuth	Magnesium	Tantalum
Cadmium	Manganese	Tin
Chromium	Mercury	Tungsten
Cobalt	Molybdenum	Vanadium
Copper	Nickel	Zinc
Gold	Platinum	
Iridium	Potassium	

11. Density. Industrial metals of importance are characterized by their high specific gravity. (Only three — aluminum, magnesium, and titanium — are below 6.) The specific gravity of commercial metals departs somewhat from the figures given in Table II, for it is very difficult to produce metals which are absolutely pure. Mechanical working of the metal, such as hammering, rolling, and drawing, has a tendency to close up the pores and compact the metal. In the liquid state all metals, with the exception of antimony and some of its alloys, are lighter than when in the solid state.

12. Crystallization. All metals tend to assume crystalline forms when they solidify. Such crystallization produces a regularity of internal structure which tends to develop cleavage planes or lines of weakness. The slower and less interrupted the cooling the more nearly perfect and regular will be the formation of the crystals. Large crystals tend to weaken a metal, and it may be stated that those metals which crystallize readily are usually weak. The mechanism of crystallization will be treated more fully in the chapter on metallography.

13. Tensile strength. The tensile strength of a metal is the greatest stress which it can withstand without rupture. The strength of a metal is profoundly affected by small amounts of impurities and by mechanical work and heat treatment. Hammering, rolling, and wiredrawing tend to increase the strength; annealing decreases it. Raising the temperature decreases the strength, while lowering the temperature increases the strength and also the hardness. Frequent application and reversal of

stresses tends to develop a diminution in strength called *fatigue*. It is believed that this is due to a rearrangement of the molecules and a consequent change in strength.

14. Hardness. There are several ways of defining hardness and as many ways of determining it. The most important are given below:

Scratch hardness is the resistance which a metal offers to scratching. We employ a conventional (Mohs) scale of ten numbers, starting with the mineral talc at 1 and ending with the diamond at 10. By experiment one can readily determine the hardness within one point.

Indentation hardness is the resistance which a metal offers to indentation. The method (Brinell) of determining it consists in forcing a hardened-steel ball, about 10 millimeters in diameter, into the smooth surface of the metal to be tested, and measuring the area of the indentation. The hardness number is the quotient obtained by dividing the pressure, in kilograms (3000 kilograms for iron and steel, 500 kilograms for softer metals), by the spherical area of the cavity formed, in square millimeters.

Rebounding hardness is measured by the rebound of a standard hard body from the metal being tested.

Cutting hardness is measured by the number of revolutions required by a standard drill, loaded with a given weight, to cut a hole of definite depth.

Of the methods given above the measurement by the Brinell method and by rebound are the most common and accurate. The temperature of a metal and the presence of small amounts of impurities greatly affect the hardness.

15. Malleability. This is the property which metals have of permanently extending in all directions, without cracking, when rolled or forged.

16. Ductility. This is the property which metals have of permanently extending by traction, or the property that enables them to be drawn into wire.

17. Fusibility. Excepting mercury, all metals are solid at ordinary temperatures. The table of physical constants gives the melting points of the more common ones.

18. Volatility. Most metals require a very high temperature in order that they may be converted into vapor. Two metals, arsenic and osmium, are changed into vapor without melting.

19. Thermal conductivity. This is the power of transmitting heat, which most metals possess to a high degree. The relative conducting powers (based on silver 100) are given in Table I.

TABLE I. RELATIVE THERMAL CONDUCTIVITY OF METALS

Silver	100
Copper	73.6
Gold	53.2
Aluminum	31.3
Lead	8.5
Platinum	8.4
Mercury	1.3

20. Commercial metals. Metals, as they are bought and sold in the open market, vary considerably in composition. Sometimes, as in the case of steel, the impurities (amounting to 2 per cent) are there because they impart desirable physical properties to the metal. On the other hand, spelter (impure zinc), as it appears on the market, may contain as high as

TABLE II. PHYSICAL PROPERTIES OF METALS

	Specific Gravity	Specific Heat at 30 Degrees Centigrade	Melting Point in Degrees Centigrade	Tensile Strength in Pounds per Square Inch
Aluminum	2.56	0.167	659	12,590 (cast) 19,290 (rolled)
Antimony	6.71	0.048	630	1,000
Chromium	6.8	0.104	1510	
Copper	8.8	0.086	1083	34,000 (bolts) 60,000 (wire)
Gold	19.3	0.032	1063	20,000 (cast) 37,000 (wire)
Iron	7.86	0.116	1520	48,000 (cast) 55,000 (rolled)
Lead	11.4	0.030	328	2,650 (cast) 1,650 (pipe)
Magnesium	1.74	0.246	651	
Mercury	13.6	0.033	− 39	
Nickel	6.7	0.109	1452	54,000
Platinum	21.5	0.032	1755	45,000 (cast) 56,000 (wire)
Silver	10.5	0.055	960	41,000
Tin	7.3	0.055	232	4,600 (cast) 5,800 (drawn)
Tungsten	19.1	0.034	3000	
Zinc	7.1	0.093	419	5,000

TABLE III. ANALYSES OF COMMERCIAL METALS EXPRESSED IN PER CENTS

	Cu	Zn	Pb	Al	Fe	Si	Cd	Mn	C	As	Sb	S	P	Cr	W
Blister copper . .	98.5		0.1		0.8					0.5	0.1	0.3			
Electrolytic copper	99.8		0.002							0.001					
Refined lead . . .	0.001	0.003	99.96		0.004						0.02				
Electrolytic zinc .		99.83	0.038		0.005		0.027								
High-grade zinc . .		99.85	0.07		0.03		0.05								
Brass special zinc .		99.0	0.60		0.03		0.50								
Prime Western zinc		97.5	1.50		0.06		0.80								
Aluminum				99.5	0.20	0.17									
Pig iron					95.0	1.00		0.30	3.50			0.05	0.08		
Wrought iron . . .					99.1	0.12		0.15	0.1			0.04	0.12		
Rail steel					98.6	0.20		0.70	0.35				0.10		
High-speed steel .					75.6	0.36		0.28	0.75			0.03		4.10	19.0

3 per cent of impurities (chiefly lead and iron), and the metallurgist would get rid of these if it could be done cheaply, for they are not desirable; but it was not until the development of the electrolytic process for reducing zinc that a strictly high-grade metal was available at a moderate price. Table III shows the degree of purity of common industrial metals.

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CHAPTER II

REFRACTORY MATERIALS

21. General. The problem of obtaining suitable refractory materials for metallurgical apparatus is one of great importance. Their uses about a metallurgical plant are legion. The walls, hearth, and roof of reverberatory furnaces, the linings of blast furnaces, cupolas, and ladles, and the checkerwork of regenerative furnaces must all be constructed of some material that will resist the high temperatures and the corrosive action of molten slag and metal. Common building materials such as brick, stone, and concrete can be used for the foundations of such apparatus, but at the temperatures employed in metallurgical operations these materials either crumble and decrepitate or melt and lose their strength.

Some of our refractories, although they have a high melting point, will react with the slags formed in the smelting operation and thus be worn away by corrosion. For this reason the character of the slag produced in any process determines the type of refractory to be used. Speaking generally, reactions which produce acid slags demand acid refractories, and those which produce basic slags demand basic refractories. There are some so-called neutral refractories which may be used for either purpose.

The chemical constituents of a slag and the lining of a furnace in which it is produced tend to form salts of a neutral character; for example, a *bisilicate* slag ($RO \cdot SiO_2$) would tend to form a *singulosilicate* ($2\,RO \cdot SiO_2$) if there were bases in the lining which it might absorb. Similarly, a basic slag, say $4\,RO \cdot SiO_2$, would, if the opportunity presented itself, extract SiO_2 from the lining to form the singulosilicate ($2\,RO \cdot SiO_2$).

22. Ideal refractory material. The ideal refractory material should resist heat, the pressure due to the load of molten metal or slag in the furnace, and the corrosive action of intensely hot slags. It should be a poor conductor of both heat and electricity and not decrepitate, or *spall*, when exposed to sudden changes

of temperature. Needless to say, no one refractory substance possesses all these desirable qualities. We must often sacrifice one in order to obtain another. The refractory materials commonly used may be divided, according to their chemical composition, into three classes, as indicated below.

23. Acid-refractory materials. These are materials which consist of silicon dioxide (SiO_2) or contain silicon dioxide as their chief constituent or in excess of the bases present. Being acid, they are used to resist the scouring, or corrosive, action of acid slags; being composed mainly of silica, they have high melting points and are used in parts of furnaces exposed to the highest temperatures. The most important are Dinas rock, siliceous sand, ganister, quartz, quartzite, siliceous sandstone, and flint.

24. Neutral materials. These are materials which are practically neutral and do not combine either with silica on the one hand, or with basic oxides on the other. Unfortunately most of them are expensive, so that they cannot be used for the complete lining of furnaces. Their chief use is as a protective course between the basic-lined hearth of a furnace and the acid-lined roof and as linings in crucibles and small furnaces used for special purposes. The most important neutral refractories are graphite, fire clay, chromite, bone ash, carbon-silicon compounds, and metals.

25. Basic materials. These are materials which contain little or no silica and resist the action of metallic oxides. The most important are magnesite, bauxite, dolomite, lime, and zirconia.

26. Melting points. The following table gives the softening points of our common refractory materials:

	Degrees Centigrade
First-class fire brick	1560
Pure kaolin ($Al_2O_3 \cdot 2\,SiO_2$)	1830
Alumina	1970
Magnesite (dead-burned)	2500
Chromite (burned iron ore)	2000
Lime (calcium oxide)	2500
Silica (SiO_2)	1830
Silica bricks	1800
Magnesia bricks	2000
Carborundum (decomposes)	2220
Carbon (becomes pliable)	1900
Carbon (becomes plastic)	2500
Carbon (boils)	3700

ACID REFRACTORIES

27. Dinas rock. This was the name given to the sandstone which was used in Wales to make the first silica bricks. The sandstone was ground and mixed with lime as a bond. Similar deposits have been developed in the United States. The following analyses show the composition of the American varieties:

	Per Cent
SiO_2	94.40–98.31
Al_2O_3	4.21–0.72
Fe_2O_3	0.70–0.18
CaO	Trace–0.22
MgO	Trace–trace
Loss on ignition	0.69–0.35

It is used in pulverulent form for the bottoms of furnaces and the linings of converters, but has even more extensive use in the form of brick.

Dinas brick, or silica brick, as it is sometimes called, is made in the following manner: The quartz or ground sandstone is mixed with the requisite proportion of calcium oxide (CaO) (usually about 2 per cent), moistened, and molded into bricks. These are first dried in a current of warm air and then carefully piled in kilns, where they are gradually brought up to a white heat. The small amount of lime present unites with the silica to form a high-melting-point silicate, which serves to bind the brick together and give it sufficient strength. It also acts as a catalytic agent in the inversion of quartz.

28. Ganister. This is the name of a siliceous rock found in south Yorkshire, England, but it has come to be used for any similar ceramic material. It contains more lime, iron oxide, and hydrated silicates of aluminum than Dinas rock, as shown by the accompanying analyses. It is therefore much more plastic.

Composition of Ganister (by Per Cents)

SiO_2	92.05–94.60
Al_2O_3	2.70–1.40
FeO	1.85–0.90
CaO	0.60–0.48
MgO	0.20–0.16
Alkalies	0.20–0.14
Water	2.00–2.60

TABLE IV. PHYSICAL AND CHEMICAL

MATERIAL (BONDED)	COMPOSITION	RESISTANCE TO BASIC FLUXES (1000°–2000° C.)	RESISTANCE TO ACID FLUXES (1000°–2000° C.)	SOFTENING POINT	FUSION POINT
Alumina . .	Al_2O_3	Readily attacked	Readily attacked	1300° C. (Inferior) 1950° C. (Best)	2050° C.
Magnesia . .	MgO	Not attacked	Readily attacked	Weak at 1300° C.	2165° C.
Silica	SiO_2	Readily attacked	Not attacked	1700° C.	1750° C.
Carbon (amorphous) . .	C	Oxidized at high temperatures	Oxidized at high temperatures	2000° C.	Crystallizes above 2000° C.
Graphite . .	C	Oxidized less readily than amorphous C	Oxidized less readily than amorphous C	2000° C.	4400° C. Sublimes @ 3900° C.
Silicon carbide	SiC	Readily attacked	Not attacked	2200° C.	2240° C.
Zirconia . .	ZrO_2	Not attacked	Fused fluorides	1850° C.	2600° C.
Chromite . .	$FeOCr_2O_3$	Not attacked	Not attacked		2050° C.
Fire clay . .		Readily attacked	Not attacked	1550° C. (Best)	1750° C.

29. Sand, quartzite, flint, etc. Sand or crushed siliceous materials are extensively used for "fettling," or repairing the walls and bottoms of reverberatory furnaces. A little clay is mixed with the crushed siliceous material so that it is slightly plastic. It can then be formed into balls, and repairs can be made to the interior of a furnace without the necessity of shutting down, — a long and expensive operation. (Of course this method can only be used for minor repairs. Once the wall or bottom is badly worn or pitted, it becomes necessary to shut down the furnace and reline it entirely with suitable brick.)

Powdered refractory materials are often used to form the bottom of reverberatory furnaces. A layer of sand about one-fourth inch thick is shoveled into the furnace and the temperature raised until the material softens and fuses together. Several layers thus fused, sometimes amounting to as much as two feet in thickness, make a strong and resistant bottom, much cheaper and stronger than when made up entirely of brick.

30. Inversion in silica brick.* While the refractoriness of a silica brick is affected by the silica content, the strength will be determined largely by the grind, the amount of glass present, and the crystal intergrowth. It has been found that under heat treatment two modifications of silica develop: one called

* M. C. Booze, in *Chemical and Metallurgical Engineering*, December 29, 1924.

PROPERTIES OF REFRACTORY MATERIALS

COEFFICIENT OF EXPANSION (LINEAR)	RESISTANCE TO SPALLING	RESISTANCE TO ABRASION	SPECIFIC GRAVITY	THERMAL CONDUCTIVITY AT 1000° C. (GRAM CALORIES PER CENTIMETER CUBE PER DEGREE CENTIGRADE PER SECOND)	DEFORMATION UNDER LOAD (50 POUNDS PER SQUARE INCH)
0.71×10^{-5}	Fair	Good	3.6	0.0068	None @ 1550° C.
1.61×10^{-5}	Poor	Very poor	3.5	0.0080	Shears @ 1410° C.
1.21×10^{-5}	Very poor	Good	2.4	0.0043	Fails @ 1700° C.
0.54×10^{-5}	Excellent	Good	1.8	0.137	None @ 1800° C.
0.78×10^{-5}	Excellent	Poor	2.2	0.277	None @ 1800° C.
4.7×10^{-6}	Excellent	Very good	3.2	0.0231	None @ 1650° C.
0.84×10^{-6}	Fair	Good	4.5	Low	Fails @ 1520° C.
1.07×10^{-5}	Very poor	Fair	3.9	0.0034	Fails @ 1450° C.
0.59×10^{-5}	Good	Good	2.7	0.0040	Fails @ 1350° C.

cristobalite, with a specific gravity of 2.27, and another called *tridymite*, with a specific gravity of 2.33. Quartz has a specific gravity of from 2.59 to 2.66. The inversion of quartz to cristobalite is accompanied by a linear expansion of 4.35 per cent; that of quartz to tridymite by an expansion of 5.3 per cent. Tridymite would thus appear to be the end product, but it is not practicable under commercial conditions to carry the inversion so far. The manufacture of silica brick consists in converting the crushed quartzite, with the aid of lime (as a catalyzer), to a structure consisting essentially of about 70 per cent of cristobalite, 25 per cent of quartz, and 5 per cent of tridymite. The after-expansion is then due primarily to the inversion of the residual quartz. Pure sandstones invert too slowly, while cherts, although they transform rapidly, have low mechanical strength. The maximum silica content is apparently between 98 and 99 per cent for satisfactory brick.

McDowell, in "A Study of Silica Refractories," shows that a certain commercial brick which was burned at 1430° C. contained 26 per cent of quartz, 4 per cent of tridymite, and 70 per cent of cristobalite. Three more burns changed these to 16, 19, and 65 per cent respectively, and he estimates that it would have required at least ten burns to produce 80 per cent of tridymite. Such treatment is not feasible in commercial work. On the

other hand, inversion in only one heat would require the kiln to be kept at a very high temperature for weeks, with an extremely high coal consumption and a considerable damage to the kiln.

31. Properties and uses. The softening point of the best silica bricks is about 1770° C. They are able to withstand ordinary furnace stresses (50 pounds per square inch) up to 1500° C. They are very hard and strong, but they have two serious defects: (1) they expand considerably when heated, so that it is necessary to provide joints (0.25 inch per foot) and tie-rods to take care of this expansion; (2) when exposed to sudden or considerable changes in temperature they flake or spall. Owing to their high porosity and to their acid character, their resistance to slagging is low. Their chief use is in roofs, walls, checkerwork, and flues not exposed to the action of slags. Other important physical and chemical properties of silica brick, as well as of other common refractory materials, are given in Table IV at the top of pages 16–17.

NEUTRAL REFRACTORIES

Fire Clays

32. General. Fire clays generally contain considerable free silica, and for that reason they are really acid substances, though they are usually classed with the neutral refractories.

A fire clay is essentially a double silicate of aluminum, consisting of the hydrous silicate of aluminum (kaolin) with silicates of the alkalies, alkaline earths, and iron. It possesses some plasticity when wet, so that it can be molded into simple shapes. It becomes hard and rocklike when burned at a red heat, and does not melt before Seger Cone No. 26 (1650° C. or 3002° F.). The leading associate mineral is quartz; in addition there are usually present small amounts of feldspar, mica, iron oxide, and colloidal and organic matter. Water is usually present, both free and chemically combined. This water is expelled temporarily when dried and permanently when burned at a red heat.

33. Kaolin. One of the principal constituents of fire clays is *kaolinite*, the common hydrosilicate of aluminum ($Al_2Si_2O_7 \cdot 2\,H_2O$)

(46.3 per cent SiO_2, 39.8 per cent Al_2O_3, and 13.9 per cent H_2O). When pure it is a soft, white, light mineral, has an unctuous feel, and is weakly plastic. It fuses at about Seger Cone No. 36 (1790° C.). It is often referred to as the clay base or the clay substance.

34. Flint clays. These correspond closely in composition to kaolin, although they may contain enough impurity to lower their refractory value. They are usually gray, and instead of being soft and chalky are hard, dense amorphous substances having little or no initial plasticity. When weathered or moistened they develop enough plasticity for ordinary molding purposes. The shrinkage on drying is slight but on burning is considerable, often causing cracking and checking. For this reason it is usually necessary to add some calcined flint clay or ground waste bricks (grog) to the mixture.

TABLE V. DOMESTIC PLASTIC REFRACTORY CLAYS*

SOURCE	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O	IGNITION LOSS
	Per Cent	*Per Cent*	*Per Cent*	*Per Cent*	*Per Cent*	*Per Cent*	*Per Cent*	*Per Cent*	*Per Cent*
St. Louis	54.64	28.75	3.00	1.85	0.30	0.35	0.15	—	11.00
Whitlock, Tennessee, No. 5	47.70	33.28	1.21	†	0.45	0.75	†	†	16.25
Mayfield, Kentucky, No. 6	60.80	24.62	0.88	2.80	0.46	0.13	0.50	0.38	10.36

† Not determined.

35. Plastic refractory clays. Most clays as they gain plasticity lose much of their valuable refractory properties. The plastic refractory clays, which unfortunately are somewhat uncommon, combine plasticity with heat-resisting power. The analyses of some common domestic clays are given in Table V. These show a higher silica and a lower alumina content than do kaolins or flint clays, the alumina being replaced by fluxes such as Fe_2O_3, MgO, and Na_2O. The purest and strongest clays are the ball clays used in the manufacture of graphite crucibles and special refractories.

36. Siliceous clays. The dividing line between refractory clays and siliceous clays has been arbitrarily fixed at 70 per cent SiO_2,

* D. M. Liddell, Non-Ferrous Metallurgy.

the extra silica being present as quartz sand. On the whole, these clays possess, in the dry state, less plasticity, bonding power, and strength than do the high-alumina clays. Their drying shrinkage and firing shrinkage are less, they are more porous and shrink less on reheating, and they have greater strength at high temperatures. They must, of course, be less refractory than aluminous clays.

Other Neutral Refractories

37. Grog. While grog is not always a natural product, it can best be described here. The term *grog* as used in the refractory industry means any calcined, broken, or ground waste product that may be used as a part of the refractory mixture. Broken fire bricks, glass pots, and material rejected during manufacture fall under this head.

38. Graphite. Carbon is not attacked by heat (under reducing conditions), has a low coefficient of expansion, and is not attacked by slags or metals. The available forms for refractory materials are charcoal, coke, and graphite. Only the last is ordinarily used, since charcoal and coke are not easily formed. The chief use of graphite is in the manufacture of crucibles and similar containers. For this purpose it is mixed with high-grade fire clay, moistened to the requisite plasticity, and molded into the proper shape for burning. Graphite crucibles contain from 25 to 75 per cent of carbon, depending upon the use to which they are to be put.

Carbon bricks have been made of graphite and clay, of coke and clay, and of coke and pitch. At present coke-pitch bricks are the only ones being manufactured. The coke is ground to about 2 millimeters, mixed with 20 per cent of tar, molded hot, air-dried for two weeks, and then baked.

39. Chromite. Chromite ($FeCr_2O_4$) is found associated with iron ores in Greece, Russia, Turkey, and California. It was first used in the lump form, but this form has been entirely replaced by bricks. Such bricks are now used very extensively in building up the bottom of copper blast furnaces, in the sides of copper-refining furnaces, and in cupolas. They are often used as a protective course between an acid roof or wall and a basic hearth or crucible. Their cost alone prevents their more

general use. Chrome brick melts at about 2050° C., becomes mechanically weak at 1450° C., is a good conductor of heat, and expands considerably upon heating. The following table gives analyses of typical ores:

ANALYSES OF CHROMITE ORES (IN PER CENTS)

	TURKEY	CALIFORNIA
Cr_2O_3	51.70	52.68
FeO	14.20	15.30
Al_2O_3	14.10	11.40
MgO	14.30	16.23
SiO_2	3.50	3.40
CaO	1.70	—
MnO	—	0.15
H_2O	0.30	0.94

To be salable, chromite should contain not less than 40 per cent of Cr_2O_3 and not more than 5 per cent of SiO_2. The shapes are made by grinding the ore to the desired fineness, mixing with lime and water to the required degree of plasticity, and then molding into bricks, which are dried and burned in ordinary brick kilns.

40. Bone ash. This is made by calcining animal bones. It consists of calcium phosphate with about 10 per cent of calcium carbonate. Formerly it was almost universally used for making cupels for assaying and for refining silver, but in recent years other materials have replaced it for these purposes.

41. Carbon-silicon compounds. Compounds such as siloxicon, carborundum, and kryptol, although important for small apparatus, are far too expensive for general use as refractory substances, nor is it likely that they will ever be so employed. Carborundum (SiC), the most common of these substances, is produced by the reduction of SiO_2 in an electric resistance furnace by means of carbon at about 1800° C.

42. Metals. Although metals have a limited use they should be classed as neutral refractory materials. The ones employed are wrought iron, low-carbon steel, cast iron, bronze and copper. If properly protected by being cooled with water, they will resist for some time the action of heat and, to a less extent, molten slag. The jackets, tuyères, and cooling plates of copper and iron blast furnaces are thus protected.

BASIC REFRACTORIES

43. Magnesite. This is probably the most valuable of our basic materials. The raw material is magnesite ($MgCO_3$), which is found in Austria, Washington, Greece, and California. Analyses of typical samples are as follows:

Analyses of Magnesite Ores (in Per Cents)

	Austria	Washington	Greece	California (Crude)
MgO	86.90	83.1	93.63	43.47
CaO	2.94	3.1	2.48	2.00
Fe_2O_3	4.68	5.0	1.05	0.80
Al_2O_3	3.47	2.0	1.00	—
SiO_2	1.67	6.8	2.24	3.86
CO_2	—	—	—	49.48

The magnesite is dead-burned to about 0.5 per cent CO_2. In the powdered form it is called grain magnesite and is used extensively for the bottoms of open-hearth furnaces. If it is to be manufactured into bricks, it is broken in crushers, ground to 1.5 millimeters, moistened with from 4 to 5 per cent of water, thoroughly pugged, molded in a hydraulic press at a pressure of 400 tons, air-dried, and burned at Seger Cones Nos. 18 to 22. These bricks usually have a red or dark-brown color from the FeO present. It is this FeO which enables the material to bond, or set, properly in the furnace. The bricks are hard and strong and stand up well. They are used for the construction of basic open-hearth furnaces, for furnaces employed for softening, refining, and cupeling lead, and for smelting, converting, and refining copper. Before the war we were dependent upon Greece and Austria for our supplies, but we are now using extensive deposits of our own in California and Washington. For a while domestic consumers preferred the foreign magnesite, claiming, with some justice, that the bricks were more durable; but at present, thanks to extensive research on the part of the brick-manufacturers, domestic bricks are quite the equal of foreign bricks.

44. Bauxite. Bauxite is $Al(OH)_3$ contaminated with varying amounts of silica, iron oxides, and other impurities, such as CaO and MgO. The variety best suited to form a refractory is

one containing little Fe_2O_3 and SiO_2. Bauxite melts at about 1820° C., but the mineral shrinks as much as 30 per cent and crumbles on calcining, so that brick cannot be made of bauxite alone. Usually SiO_2 is added to counteract this shrinkage. Every manufacturer has his own formula and makes various and often extravagant claims for his particular brick. One with 57.76 per cent of Al_2O_3, 39.75 per cent of SiO_2, 2.30 per cent of Fe_2O_3, and 0.54 per cent of MgO melted at Seger Cone No. 37 and stood up well as a basic lining. Bauxite fused in the electric furnace forms a popular refractory called alundum.

45. Dolomite. Dolomite is a magnesian limestone. The normal dolomite, $(Ca \cdot Mg)CO_3$, contains 21.7 per cent of MgO and 30.4 per cent of CaO. The composition varies a great deal, but, other things being equal, the richer in MgO the more valuable the stone. The composition of a typical dolomite is given below:

	Per Cent
CaO	30.36
MgO	20.43
SiO_2	3.65
FeO	0.91
CO_2	—
Al_2O_3	0.71

Being strongly basic in character, dolomite resists well the action of basic slags and is extensively used as a repair material for the linings of basic open-hearth furnaces. The dolomite is calcined in cupolas, or shaft furnaces, until substantially all the CO_2 has been expelled. Formerly it was made up into bricks, but these have not proved entirely satisfactory, and today most of the dolomite is used in the grain form. It has not as high a melting point as quicklime, which is practically infusible, but quicklime is easily affected by the moisture of the atmosphere and is not sufficiently coherent to be easily handled or formed.

46. Zirconia. The refractory properties of zirconia have been known for a number of years, but until recently no deposit of sufficient size had been developed so as to make its use practicable. The chief source at present is Brazil. Zirconia is one of the most refractory substances known. It is not attacked by the oxygen of the air, like graphite, nor is it corroded by molten silicate slags. In a pure state its melting point is in the neighborhood of 3000° C., and even when it contains as much

as 1.25 per cent of silica and iron oxide it does not melt below 2560° C. The analysis of an average sample is given below:

	Per Cent
ZrO_2	84.1
Fe_2O_3	3.1
SiO_2	7.7
TiO_2	1.2
Al_2O_3	0.7

Zirconia does not lend itself to the manufacture of brick; for it has but little plasticity, and the use of much clay as a binder lowers its melting point and develops excessive fire shrinkage.

The initial cost of a zirconia lining, while high as compared with magnesite, is often more than compensated for by its resistance to corrosive slags, metals, and metallic oxides, its high melting point, and its low thermal conductivity. It is in more extensive use abroad than in this country. One authority cites the performance of an open-hearth furnace which was still in good condition after a campaign of over four months. Even in this country it is being used in the lining of electric furnaces and in the manufacture of crucibles and containers. The low thermal conductivity and high tensile strength enable one to make use of thin-walled sections.

47. Crucibles. Strictly speaking, the term *crucible* is applied only to open-mouthed vessels in which metals or other materials are heated in furnaces, and which can be handled by means of tongs. The term is also applied to the hearth of a copper or iron blast furnace.

48. Fire-brick manufacture. Fire brick is the most common refractory material in use about metallurgical plants; so its manufacture will be discussed in a brief way. While many of the sizes have become standard, as indicated in Fig. 1, there are many special shapes used in coke-retorting, zinc distillation, iron blast furnaces, recuperators, and regenerators. In the manufacture of fire brick five steps have to be considered: composition of the mixture, preparation, molding into the desired shape, and drying and burning of the brick.

The mixtures ordinarily used for making fire brick consist of refractory raw clay, burned flint clay, and raw refractory plastic clay. The flint clay, which is both abundant and cheap, makes up the largest part of the mixture. Since it shrinks considerably

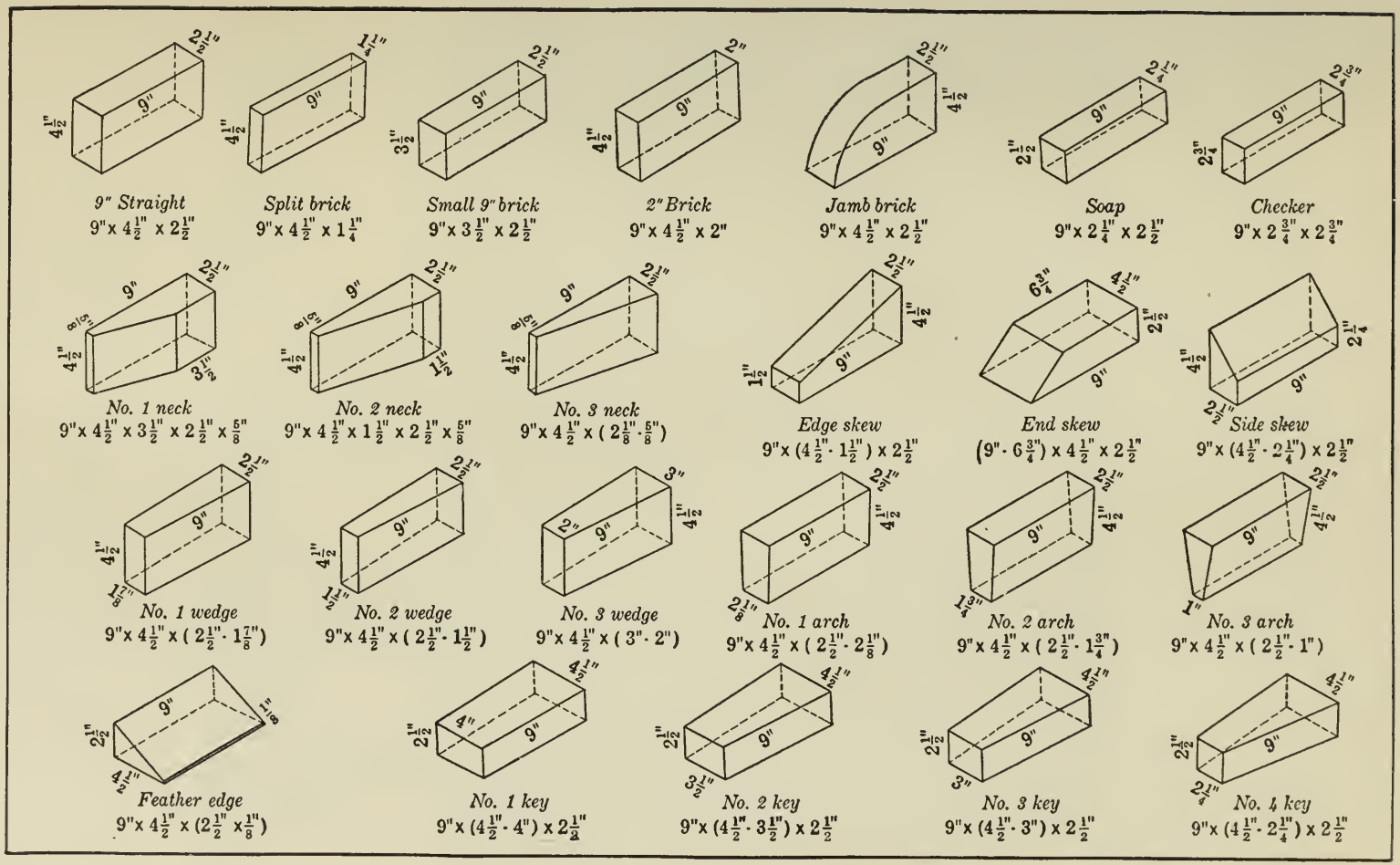
9" Straight
9" x 4½" x 2½"
Split brick
9" x 4½" x 1¼"
Small 9" brick
9" x 3½" x 2½"
2" Brick
9" x 4½" x 2"
Jamb brick
9" x 4½" x 2½"
Soap
9" x 2¼" x 2½"
Checker
9" x 2¾" x 2¾"
No. 1 neck
9" x 4½" x 3½" x 2½" x ⅝"
No. 2 neck
9" x 4½" x 1½" x 2½" x ⅝"
No. 3 neck
9" x 4½" x (2⅛" · ⅝")
Edge skew
9" x (4½" · 1½") x 2½"
End skew
(9" · 6¾") x 4½" x 2½"
Side skew
9" x (4½" · 2¼") x 2½"
No. 1 wedge
9" x 4½" x (2½" · 1⅞")
No. 2 wedge
9" x 4½" x (2½" · 1½")
No. 3 wedge
9" x 4½" x (3" · 2")
No. 1 arch
9" x 4½" x (2½" · 2⅛")
No. 2 arch
9" x 4½" x (2½" · 1¾")
No. 3 arch
9" x 4½" x (2½" · 1")
Feather edge
9" x 4½" x (2½" x ⅛")
No. 1 key
9" x (4½" · 4") x 2½"
No. 2 key
9" x (4½" · 3½") x 2½"
No. 3 key
9" x (4½" · 3") x 2½"
No. 4 key
9" x (4½" · 2¼") x 2½"

FIG. 1. Commercial fire-brick shapes

upon drying and burning, and thus has a tendency to crack and lose its shape, part of it is always calcined. As the flint clay furnishes the fire-resisting power and the plastic clay the physical strength to the brick, it will be seen that it is not possible to make a brick that will have the desirable qualities of both.

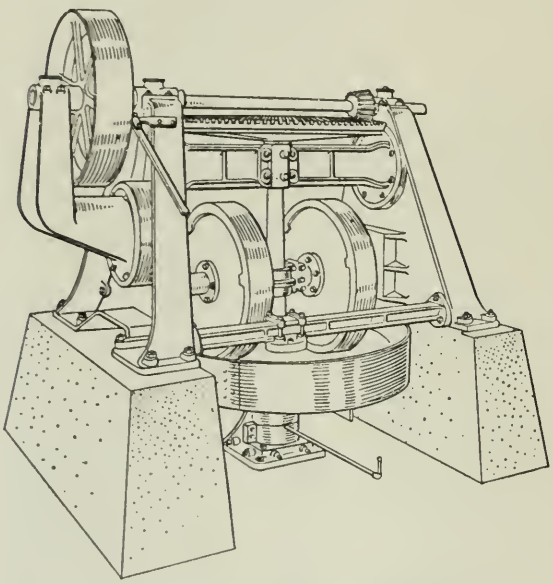

FIG. 2. Dry pan

A brick that is to resist intense heat will consist of about 45 per cent (by volume) of raw flint clay, 45 per cent of calcined flint clay, and 10 per cent of plastic clay. Such a brick is loose and porous and has not much physical strength. On the other hand, a brick that is to be physically strong will consist of a mixture of about 50 per cent (by volume) of raw and calcined flint clay and 50 per cent of plastic clay.

Even the best clay deposits are not entirely uniform, and it is usually necessary to sort the clay into different grades and perhaps subject it to a preliminary breaking to rid it of various impurities, such as iron oxide, silica, or pyrite. Most

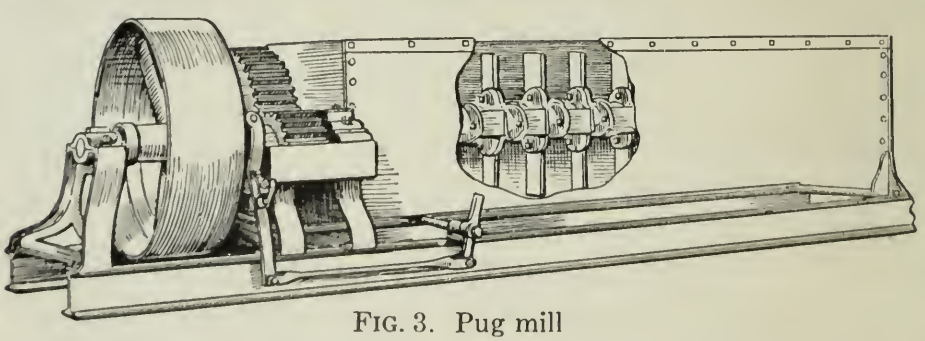

FIG. 3. Pug mill

clays are washed in a log washer or other simple type of disintegrating or stirring device, and the washed clay is recovered in purer form by settling or by filter pressing. Often the clay is spread out on floors and weathered for some months, since it has been found that this treatment makes it more

uniform and increases its toughness and plasticity. The mixing is done either in a dry pan, as shown in Fig. 2, or in a wet pan with water. It is then tempered in some form of pug mill, as shown in Fig. 3. From the pug mill the mixture is fed by a screw into a die which forces it out into a ribbon of the desired cross section onto a cutting table, where it is automatically cut into bricks of the desired size.

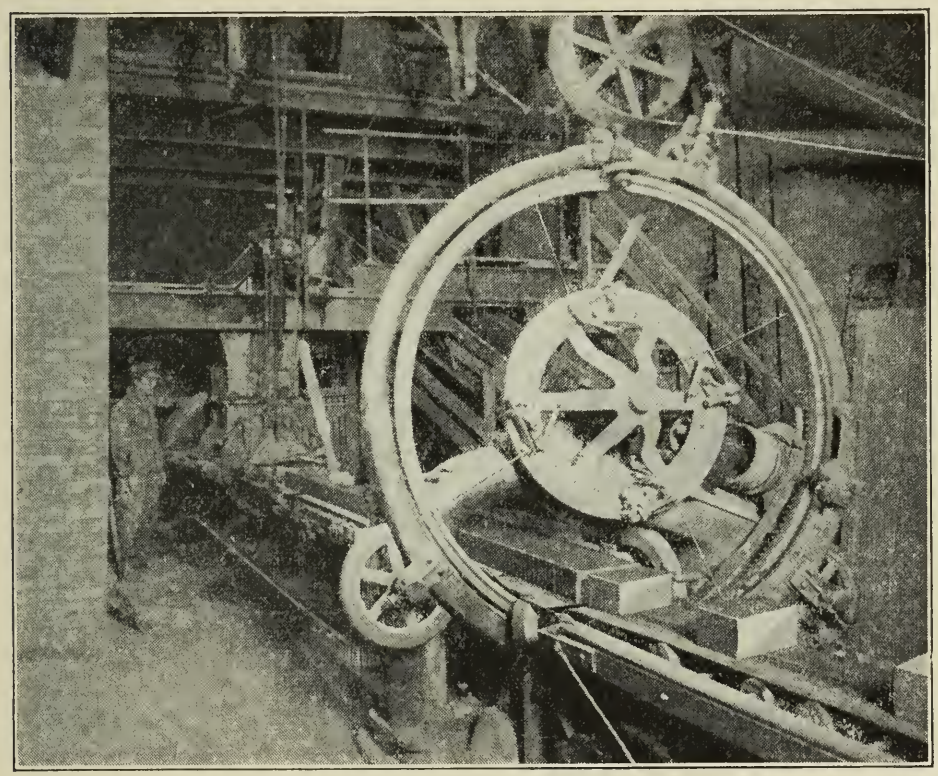

FIG. 4. Stiff-mud machine

Bricks are molded either by hand or by machine. For the best fire brick, the temper of which has to be especially soft, the bricks are molded by hand in small wooden molds holding from two to six bricks, depending upon the size. In machine molding there are distinguished the soft-mud process, the stiff-mud process, and the dry process. A soft-mud machine consists of a vertical pug mill which repugs the mixture and delivers it to sanded molds. The bricks are rough and unfinished and usually have to be re-pressed. The soft-mud process and the dry process are used chiefly in briquetting, seldom in the manufacture of fire brick.

The bricks must be carefully dried before being burned. This process is carried out either on drying floors heated by flues or steam pipes passing underneath, or in tunnel driers. No general figures for time can be given, since this varies with the size of the brick and the mixture of which it is composed.

The dried fire bricks are then removed to brick kilns, where they are burned. These are classed as down-draft, up-draft, and continuous kilns, according to the methods of firing. A

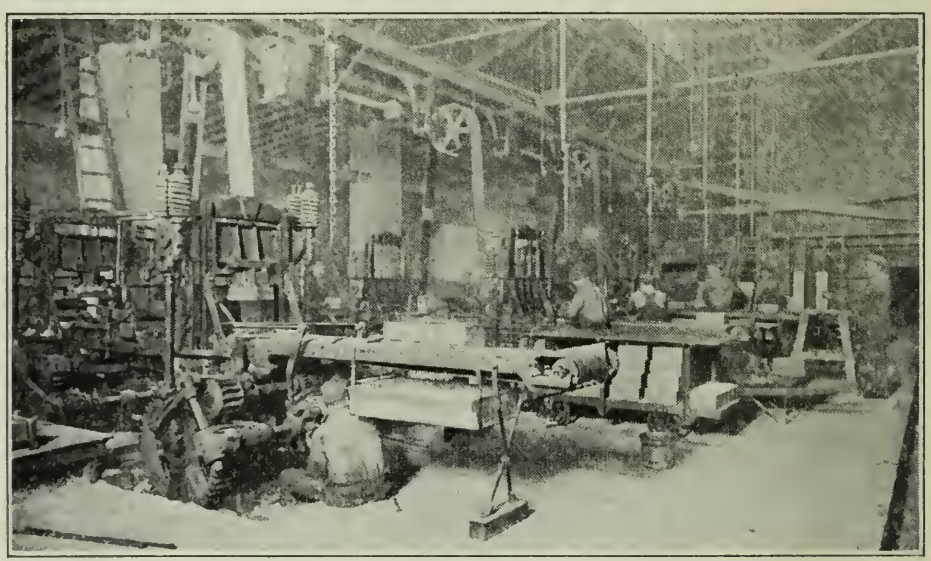

FIG. 5. Sizing machine

down-draft kiln with a central stack is shown in Fig. 6. This is the common type in use in burning fire brick. This furnace has a number of fireplaces at the periphery. The flames, upon entering the kiln, rise in the vertical flues to the top of the kiln, spread over the tops of the bricks, and descend, in the open space left between them and through the perforated bottom on which the bricks rest, into underground flues connected with the main chimney. Under ordinary conditions the waste heat from these kilns is often used in the tunnel driers to dry the raw brick. The temperature is kept at Seger Cones Nos. 9–12 (1310° to 1370° C.) for from five to seven days. It takes a furnace about the same length of time to cool. To aid in the cooling, air is sometimes passed through the kilns and then used for drying the bricks, thus increasing the efficiency of the plant.

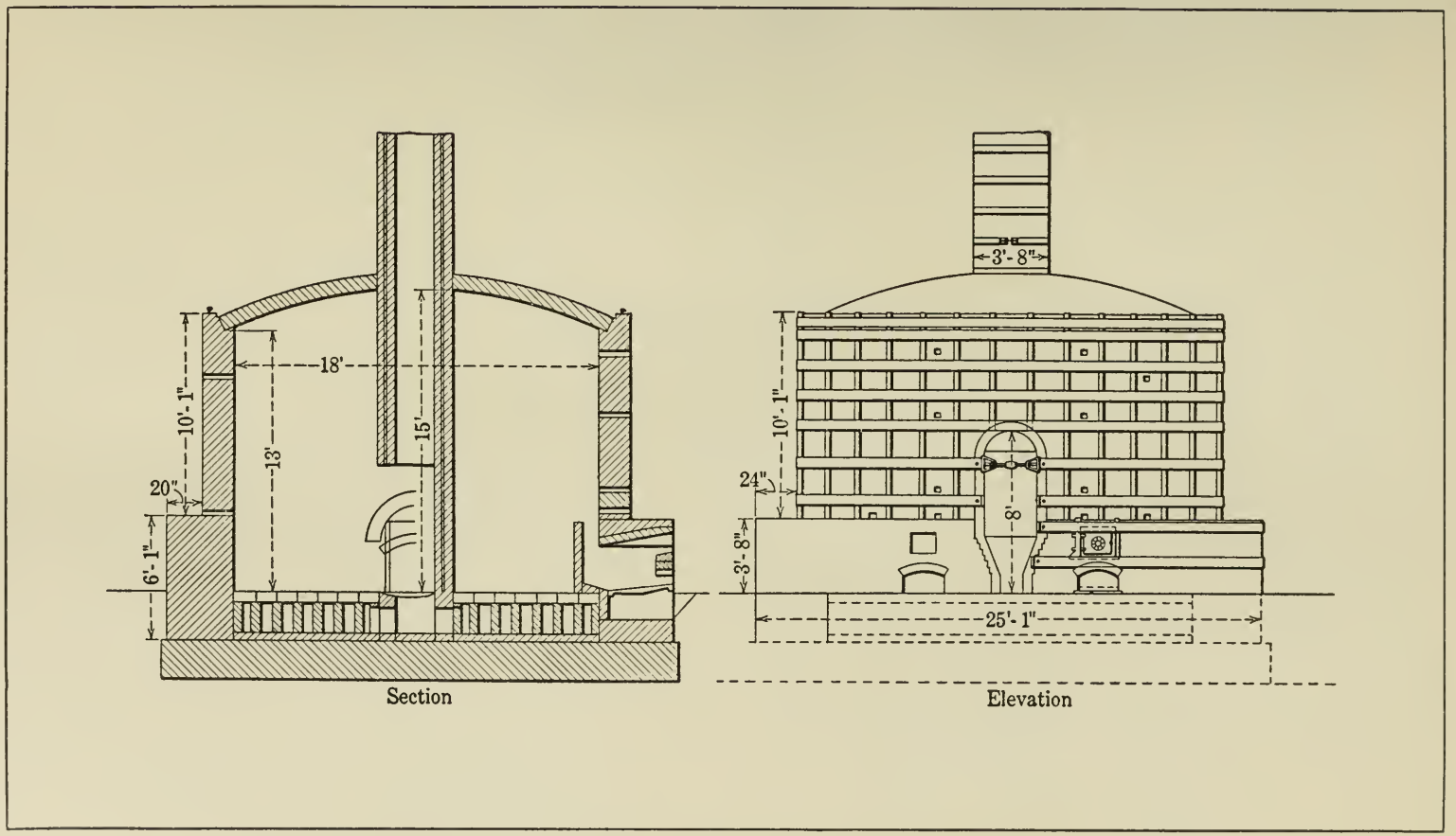

FIG. 6. Down-draft kiln

49. Seger cones. In many metallurgical operations, and especially in the ceramic industry, it has been found more practicable to determine temperature by means of Seger cones than by electrical or optical pyrometers. Seger cones are three-sided pyramids: Nos. 022–25 are 3 inches high with a base $\frac{5}{8}$ inch wide; Nos. 26–42 are $\frac{2}{3}\frac{5}{2}$ inch high with a base $\frac{3}{8}$ inch wide. They are made of mixtures containing varying proportions of Na_2O, PbO, B_2O_3, and Al_2O_3 in the case of the lower melting points, and of varying proportions of Al_2O_3 and SiO_2 in the case of the higher melting points. The last cone (No. 42) is made of pure Al_2O_3, which melts at 2050° C. Some of the other points along the scale are indicated in the following table:

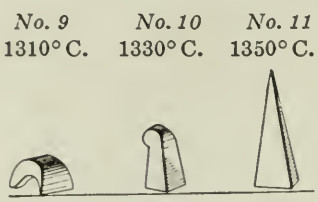

FIG. 7. Seger cones

NUMBER OF CONE	SOFTENING TEMPERATURE IN DEGREES CENTIGRADE	SOFTENING TEMPERATURE IN DEGREES FAHRENHEIT
1	1150	2102
10	1330	2426
15	1430	2606
20	1530	2786
26	1650	3002
30	1730	3146
35	1830	3326
42	2050	3722

To determine the temperature of a kiln or a furnace it is necessary to use at least three cones. For example, if we knew that the approximate temperature of a kiln or a furnace was 1300° C., we should place, on a brick in the kiln or on a suitable support in a furnace, Cones Nos. 9, 10, and 11. Suppose that Cone No. 11 did not fuse at all, that Cone No. 10 "sweated," and that Cone No. 9 turned down, we should know that the temperature was about 1330° C. The temperature indicated for each cone is only approximate; it is supposed to have been reached when the cone assumes the position of No. 10 in Fig. 7. Since it is exposed to the same furnace conditions as the substance being treated it often furnishes a better measure of the temperature than a pyrometer.

50. Prices. The range in prices (1927) of common refractory materials is indicated on the following page:

	Price per Thousand	Price per Ton
Fire brick, Illinois		
First quality	$43 to $46	—
Second quality	$35 to $38	—
Ground fire clay	—	$7
Silica brick, Chicago	$52	—
Silica clay	—	$8 to $10
Magnesite brick, Chester, Pennsylvania	—	$65
Grain magnesite, Chester, Pennsylvania	—	40
Chrome brick	—	45
Bauxite brick	140	—
Zircite	—	60
Graphite (lump)	—	160

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CHAPTER III

FUELS

51. General. A fuel may be defined as any solid, liquid, or gaseous substance which, being rapidly burned in air, evolves heat capable of being applied to industrial purposes. The most common heat-producing substances are carbon, in the form of wood, charcoal, coal, or coke, and various hydrocarbons such as fuel oil and natural gas. For combustion to begin and continue, the material must be brought to the kindling temperature (ignition point) of the material. This varies from about 225° C. in the case of dry peat up to 640° C. in the case of certain enriched producer gases. When a fuel is once ignited, combustion will continue if the heat evolved is sufficient to keep the temperature of the substance above this ignition point; otherwise combustion will cease as soon as the external source of heat is withdrawn. Combustion is said to be perfect when the constituents are brought to the highest state of oxidation, or, what amounts to the same thing, to that state evolving the largest amount of heat. It is imperfect when they are brought to a lower state than this. The conditions necessary for perfect combustion are (1) that air in sufficient quantity be brought in intimate contact with the combustible material; (2) that the temperature be high enough so that combustion can be maintained throughout the mass; (3) that it be given sufficient time in which to act. It is easier to mix a gaseous fuel than a solid one, and consequently combustion is more nearly perfect with a gaseous fuel, since there is less excess of air. In the case of a solid fuel the amount of excess air needed depends upon the porosity of the charge and upon its purity. The caking, sintering, and crumbling of solid fuels hinder the free access of air and produce imperfect combustion.

The combustion of a fuel is usually attended by the emission of light, which varies from a long, luminous flame, in the case of gases or solid fuels containing large percentages of hydro-

carbons, to a simple glow in the case of coke or charcoal. According to the amount of combustible gas evolved, we distinguish between long-flame and short-flame fuels.

Theoretically the flame from a fuel, or the atmosphere above a burning fuel, may be either oxidizing, reducing, or neutral, according to the relative proportions of gaseous substances present. Practically, however, such close control is not possible. An oxidizing flame is readily obtained in any metallurgical furnace, a reducing flame at best can only be approximated, while a neutral flame has only an imaginary existence. The flame of a burning fuel is due to two causes: either the carbon is burning with an insufficient amount of air, forming CO, which in turn burns with a flame to CO_2, or the CO_2 initially formed is being reduced to CO by coming in contact with the incandescent carbon, and this CO burns to CO_2 as before.

The heat generated by combustion may be transmitted through the fuel by either radiation or contact. Gaseous fuels transmit heat mostly by radiation, while solid fuels do this by contact.

52. Calorific power. The *calorific power* of a fuel is the amount of heat evolved by a given weight of the fuel under conditions of perfect combustion. It is independent of the time taken. Both the *British thermal unit* and the metric unit, or *gram-calorie unit*, are used. This calorific power can be found either by calculation or by experiment in the laboratory. The results by calculation, while interesting from a theoretical standpoint, are not usually employed in practice. Fuels are bought and sold on calorimetric determinations. The *calorific intensity* of a given fuel is the degree of heat evolved by a given weight of fuel in perfect combustion, in air, under standard conditions of temperature and pressure.

53. Proximate analysis. In a *proximate analysis* an attempt is made to group the constituents of the coal according to certain physical properties that are technically important, both in the sale and purchase for fuel and in the classification of coals. Such an analysis is applicable to all forms of solid and liquid fuel, with such slight modifications as are required by the physical properties of the fuel being investigated. The usual items included in a proximate analysis are moisture, volatile matter, fixed carbon, ash, and sometimes sulphur. The expressions

"fixed carbon" and "volatile matter" require explanation, for they are really only relative terms. If a carbonaceous fuel is heated to redness (in a retort), the heat will decompose a portion of the coal substance, a part coming off as a thick, black, tarry smoke and a part remaining behind as a solid residue. All the gases thus evolved in the process are termed volatile, while the residue remaining behind in the container consists of ash and a material which is largely carbon. This is called the fixed carbon. The relative percentages evolved will vary widely, according to the conditions of the analysis and the character of the coal. It is very important, therefore, that all chemists use the same method in order that their results may be correlated. The methods now in use have been standardized by a joint committee of the American Chemical Society and the American Society for Testing Materials.

54. Ultimate analysis. In an ultimate analysis the aim is to report as accurately as possible the percentages of chemical elements in the fuel, without any attempt to indicate the manner in which they are combined. The elements usually reported are carbon, hydrogen, nitrogen, oxygen, phosphorus, and sulphur.

55. Classification of fuels. Fuels are conveniently classed (after Hofman) under the following heads:

SOLID FUELS

Natural: wood, peat, bituminous coal, anthracite.
Prepared: pulverized fuel, briquettes, coke.

LIQUID FUELS

Natural: petroleum.
Prepared: distilled oil.

GASEOUS FUELS

Natural: natural gas.
Prepared: producer gas, blast-furnace gas, water gas, coal gas.

56. Solid fuels in general. All natural solid fuels are of vegetable origin. The younger fuels, such as wood and peat, are being formed today; bituminous coals were formed many ages ago and are still undergoing slight though very slow change; the anthracites have reached the end of the process of carbonization. The color of the material in this metamorphism changes from the white of wood to yellow, to brown, and finally to the black of anthracite.

Prepared solid fuels are becoming a larger and larger factor in our industrial-fuel situation. Pulverized coal has the advantage of the utilization of low-grade fuels, more nearly perfect combustion, and ease of handling. There are some installations that do not lend themselves to the use of this fuel. In such cases we are resorting to the compressing, or briquetting, of finely divided combustible material. Carbonized fuels such as charcoal and coke have a field all their own in metallurgical work. They are essential to the operation of copper, lead, and iron blast furnaces and to all processes in which heat and a reducing atmosphere are needed at the same time. The following table gives a classification of some of our common fuels:

	Chemical Composition			Fixed Carbon	Calorific Power in Calories
	C	H	O		
	Per Cent	*Per Cent*	*Per Cent*	*Per Cent*	
Cellulose ($C_6H_{10}O_5$)	44.44	6.17	49.39	28.30	3600
Wood	50	6	44	30–35	4000
Peat	58	6	36	35–40	4500
Brown coal (lignite)	65–75	6–4	29–21	40–50	5000–8000
Bituminous coal (coking)	88–91	5.5–4.5	6.5–4.5	74–82	9300–9600
Bituminous coal (noncoking)	75–80	5.5–4.5	19.5–15	50–60	8000–8500
Anthracite	93–95	4–2	3	90–92	9000–9200

57. Wood. Since the discovery of coal, wood has become of minor importance to the metallurgist and is used today only for special purposes or where coal or coke is too expensive.

58. Peat. Peat represents the first step in the formation of coal. It usually takes the form of an accumulation of more or less decomposed vegetable matter in a bog or a swamp. The older and thicker this deposit the farther will decay have progressed and the denser and harder will be the peat. Peat when dug is wet, containing as much as 80 per cent of water; when air-dried it may contain from 15 to 20 per cent. It is hygroscopic, so that the last bit of water cannot be expelled permanently. The ash content varies greatly: from 5 to 10 per cent is a low figure; from 10 to 20 per cent, not uncommon. Since the water content also varies widely, no general figures can be laid down as to calorific power. A peat with from 25 to 30 per cent of moisture and from 6 to 8 per cent of ash would have a calorific power of about 3000 calories. It is not used in the

metallurgical industry in this country, but abroad, particularly in Germany, it is molded into briquettes and burned in furnaces.

59. Brown coal (lignite). Brown coals comprise that class of fuels which are a little older than the peats and yet have not been metamorphosed to that point represented by the bituminous coals. Trunks of trees, plants, and ferns are still recognizable in lignites. When mined they may contain as much as 50 per cent of water, and they can never be dried much below 10 or 15 per cent. The amount of ash will vary much as it does in peat, from 4 per cent up to as much as 15 per cent. Lignites containing more than 20 per cent of ash are not of much value as fuels. The calorific power of a lignite free from water and ash is from 5000 to 5500 calories; that of a lignite 30 per cent water and 10 per cent ash is about 3300 calories, of which not more than 70 per cent is available in ordinary use. Like peat, lignite is of little value in metallurgy, for it has neither the strength to resist pressures in blast furnaces nor sufficient concentration to make its use economical.

60. Bituminous coal. Bituminous coal represents the next step in the process of carbonization. All traces of the remains of the leaves, ferns, and trees have disappeared. It is darker, softer, more friable, heavier, and richer in carbon than the brown coals. The fracture is conchoidal to uneven, and the coal breaks parallel to certain bedding planes. Its specific gravity, when it contains but little ash, varies from 1.25 to 1.35. Table VI shows the properties and analyses of some typical American bituminous coals.

TABLE VI. DOMESTIC BITUMINOUS COALS

(Compositions expressed in per cents)

State	Moisture as Received	Proximate Analysis			Ultimate Analysis					Loss in Air Drying	Calorific Value	
		V. M.	F. C.	Ash	S	H	C	N	O		Cal.	B.T.U.
Alabama	3.34	34.72	56.98	8.30	1.08	4.99	77.35	1.34	6.94	1.8	7758	13,964
Colorado	5.32	38.33	52.39	9.28	0.80	4.93	71.57	1.67	11.75	3.0	7290	13,122
Illinois	5.56	36.44	54.33	9.23	3.04	4.81	72.80	1.38	8.74	3.6	7437	13,386
Pennsylvania	2.60	33.54	61.00	5.46	0.79	5.24	80.25	1.49	6.77	1.4	8034	14,461
Pennsylvania	1.44	35.12	58.61	6.27	0.79	5.14	79.91	1.46	6.43	—	8028	14,450
West Virginia	3.13	34.02	58.24	7.74	0.93	5.16	77.41	1.54	7.22	1.6	7745	13,941

The amount of water present averages 5 per cent. The percentage of ash in high-grade bituminous coal ranges from 4 to

7 per cent; in ordinary coal, from 7 to 14 per cent. The sulphur ranges from 1 to 3 per cent, with 2 as the more common figure. Coal for the manufacture of blast-furnace coke must be low in this impurity, since most of the sulphur enters the pig iron and imparts undesirable qualities to it. This sulphur occurs in combination with iron as pyrite, with calcium as gypsum, and in organic matter.

61. Pulverized coal. In the mining operation a great deal of fine coal is unavoidably produced. Formerly this was a waste product, since its nature made it difficult to burn it under boilers like other solid fuels. In the past few years furnaces have been devised to burn this material successfully, — so successfully, in fact, that today we pulverize an increasing percentage of our solid fuels. This method of burning certain coals has several important advantages. In order to work satisfactorily it is necessary that the volatile hydrocarbons of the coal be over 30 per cent, that the moisture be uniform and not exceeding about 1 per cent, that the coal slack be finely and uniformly pulverized and intimately mixed with the necessary amount of air for perfect combustion, and that feeding be continuous and uniform. Short-flame coals with less than 20 per cent volatile hydrocarbons do not ignite well.

The preparation of pulverized coal is carried out as follows: Run-of-mine coal is dried to about 1 per cent moisture and broken in rolls to about $\frac{1}{4}$ inch in diameter. It is then fed into some type of pulverizer (the Raymond Roller Mill is one in common use for this purpose). The grinding apparatus is surrounded with an air-tight hopper, under suction, so that the material, as soon as it is reduced to a certain limiting size, is drawn away by the current of air passing through the machine. Coarse particles escaping without having been ground are automatically returned to the machine. The coal must be so finely pulverized that 85 per cent of it will pass through a 200-mesh screen.

62. Coking. If coal is heated in a closed vessel, so as not to be oxidized by the oxygen of the atmosphere, it gives off volatile matter and leaves behind a residue of fixed carbon. Some coals, when treated in this way, soften, fuse, and swell into a spongy mass. Finally, when all the volatile matter has been expelled, it solidifies into a coherent, grayish-black, cellular mass which we call coke. A noncoking coal, on the con-

trary, changes its appearance only slightly and leaves behind a sandy residue which has no further value as a fuel.

Between the two there are numerous gradations. Although there are a great many theories concerning this phenomenon of coking, it has not been satisfactorily explained. The old theory that the tar given off cements the coal into a coherent mass is not tenable. The ratio of hydrogen to oxygen in the coal appears to be more favorable. It has been found that coals with an H to O ratio of 59 per cent or over show good coking qualities; a ratio of 55 per cent gives fair coke, while 50 per cent yields poor coke if any at all. The ultimate analyses teach us that a coal either high in carbon or high in oxygen will not coke. Unfortunately this rule is not universal, for a certain coal with volatile hydrocarbons 24.58, fixed carbon 68.02, ash 7.40, S 0.76, and P 0.006 per cent gave a sandy residue, while a coal from another district with volatile hydrocarbons 24.36, fixed carbon 67.84, ash 7.80, S 0.89, and P 0.004 per cent gave an excellent coke. Tests alone can decide the matter. Tables VII and VIII show the ultimate analyses and physical properties of some domestic cokes.

TABLE VII. ULTIMATE ANALYSES OF COKE*

SAMPLE	C	H	O	N	ASH	S
A	91.77	1.23	0.04	—	6.0	0.933
B	85.84	0.52	1.0	0.380	11.4	0.86
C	80.85	0.51	2.1	—	16.0	0.51

TABLE VIII. PHYSICAL PROPERTIES OF AMERICAN COKES*

LOCALITY	WEIGHT IN POUNDS PER CUBIC FOOT (DRY)	SPECIFIC GRAVITY	FIXED CARBON	H_2O	ASH	S	P	VOLATILE MATTER
Connellsville, Pa.	47.69	1.80	86.88	0.79	11.54	0.70	0.05	1.31
Pocahontas, Va.	59.68	1.83	92.64	0.35	5.82	0.74	0.006	3.41
Blocton, Ala. .	54.56	1.75	92.76	0.15	6.94	0.74	0.007	0.81

63. Charcoal. When wood is subjected to destructive distillation it gives off volatile matter which consists of hydrogen, various hydrocarbon gases, pyroligneous acid, and tar. There

*H. O. Hofman, General Metallurgy.

is left behind in the retort a black, lustrous, carbonaceous residue which is termed charcoal. It often retains the structure of the wood from which it was made. The ultimate composition of charcoal is given in the following table:

Condition	C	H	O	Ash	Water
Air-dry	84.5	2.5	4.3	1.2	7.5
Water-free	91.3	2.7	4.8	1.2	—

The calorific power of ordinary charcoal is from 6000 to 7000 calories.

64. Charring. Formerly most of the charcoal was made by charring in heaps. This is a very simple method but is wasteful both of charcoal and of the valuable by-products, such as calcium acetate and methyl alcohol. In this method, wood cut to the proper length (usually cord-wood size) is piled in heaps about 20 feet in diameter and 10 feet in height. The heap is then covered with a layer of sod, dirt, or earth in order to protect it from the air and prevent too rapid oxidation. Such a charring heap is shown in Fig. 8. The heap shrinks from 15 to 25 per cent in the charring process and causes cracks to appear in the cover. These must be sealed with moist earth. The pile is ignited at the center and, after a brisk fire is burning, is sealed over, and the cover is so manipulated that only sufficient air for charring will be admitted. It will take from seven to twelve days to char a heap of this size. When the charring is finished, the heap is covered with moistened loam in order to cool it and to smother the fire. In a day or two the heap will be cooled sufficiently so that the red-hot logs may be drawn from the fire with a rake and quenched with water. The yield by volume is from 50 to 60 per cent of the wood used; by weight it is from 22 to 23 per cent.

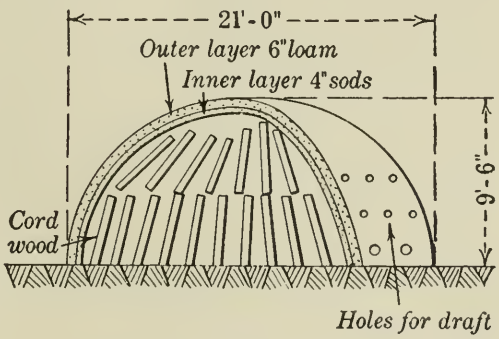

Fig. 8. Charring heap

The next logical step is to replace the cover of soil with one of brick or some other more resistant material, connect it to a

flue, and endeavor to collect and save some of the valuable gases. Such a structure is called a *stall* or *kiln*, and until recently most of the charcoal (where large quantities are handled) was produced in this way. Stalls may be rectangular, cylindrical, or conical in shape. They have stone or cement foundations, floors made gas-tight with a fire-clay mixture, and walls of red brick laid in clay mortar and whitewashed to make them air-tight and to aid in disclosing leaks. Conical or cylindrical stalls are built to hold from 60 to 80 cords of wood. The wood is charged in horizontal layers around a circular chimney space, and usually a horizontal kindling flue is left near the bottom. The modes of lighting and charring are similar to those employed in heaps. The gas and fume are sucked off by means of a fan into the flue and are conducted to the main condensation plant, where the valuable by-products are recovered. The 60 cords of wood in the standard charge will yield 10 per cent of brands, 48 bushels of charcoal, 200 gallons of acid liquor with 2 per cent methyl alcohol, 250 pounds of tar, and 12,000 cubic feet of gas.

At the present time *retorts* are used a great deal in the manufacture of charcoal, for the by-products are now nearly as valuable as the charcoal. Furthermore, quick charring may be carried on in a retort, and such quick charring is favorable to the recovery of a high percentage of the volatile hydrocarbons. The charcoal is weaker, but since little of this is used as a metallurgical fuel, such a defect is of minor importance. The retort consists of a horizontal steel shell 46 feet long, 6 feet wide, and 8 feet high, closed at both ends by gas-tight swinging doors. Running through the retort is a standard gauge track carrying the charring trucks. As the trucks of charred material are taken from the retort another train of trucks carrying wood is placed in the retort, and thus most of the heat is conserved.

Stalls and retorts have the advantage over heaps in that the valuable by-products are recovered. The leading advantages of retorts over stalls are a high yield in charcoal, methyl alcohol, and acetic acid, a more uniform quality of charcoal, and a lower cost of operation.

65. Coking. The coking of coal may be carried on in heaps, in open or closed stalls, or in retorts. The manner of coking is dependent on the character of the coal and on whether or not

the operator wishes to save the by-products. It is encouraging to note in this connection the very rapid strides made by retorts in recent years, for it is nothing less than an economic crime to employ the beehive oven for coking purposes. In general it may be said that it is difficult to obtain a satisfactory blast-furnace coke from a coal which contains over 28 per cent of volatile matter. Different grades of coal are usually mixed, or blended, in order to obtain a more desirable or uniform coke. It is frequently necessary to wash or dress the coal in order to reduce the amount of ash or sulphur.

The method of coking in heaps is no longer used in this country or, to any great extent, in Europe. It requires lump

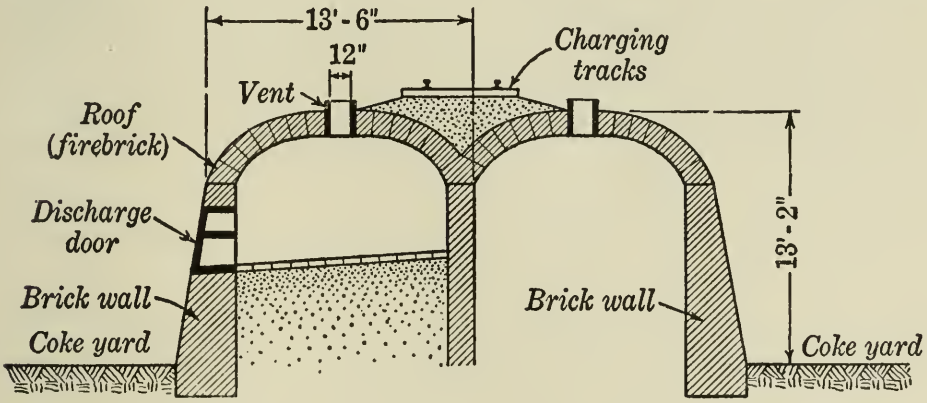

FIG. 9. Beehive coke ovens (staggered ovens)

coal and gives a small yield of coke, and this coke is often dirty and not uniform in either size or quality. The operation consists in piling the coal around a central chimney, kindling the pile at the bottom, and checking combustion by a cover as in charring charcoal.

The closed stalls used in the manufacture of coke usually take the form of the ordinary "beehive." Such a beehive is shown in Fig. 9. It is a dome-shaped structure, 12 feet in diameter and 7 feet in height, with walls of siliceous brick 9 inches thick. It will hold about 6 tons of coal. It has two openings: one in the side, at the bottom, where air is admitted for combustion and the coke is withdrawn; the other in the center of the top, for charging the coal and to serve as an outlet for the gases of combustion. If a beehive has been working normally, the cycle of operations is about as

follows: When the coke has been drawn, a new charge of from 5 to 6 tons is dropped through the opening in the crown, leveled off, and the front bricked up to within 2 inches of the top and sealed. This will form a charge about 2 feet deep in the oven. There is sufficient heat in the oven to ignite this charge and start distillation. Coking will be finished in about forty-eight hours. The coke will then be drawn out, quenched, and loaded into cars.

In coking in retorts the coal is treated in an oblong, narrow retort lined with silica brick or some siliceous refractory material. The coal is subjected to destructive distillation by burning all or part of the volatile matter derived from the coal in flues surrounding these retorts. Air is completely excluded from the retort during distillation. A number of retorts (from twelve to twenty, depending upon their size) are united to form one block, in order to reduce to a minimum the loss of heat by radiation. The retorts in common use today are the Koppers, Semet-Solvay, and Hoffmann.

66. Koppers oven. The Koppers oven for retorting bituminous coal is shown in Figs. 10 and 11. The retort proper, *e*, is about 40 feet long, 11 feet high, and 19 inches wide. It contains, under normal conditions, about 15 tons of coal. Retorting will consume from fifteen to twenty hours, depending upon the temperature of the retort and the character of the coal. Underneath each retort is a regenerative checkerwork for heating the air and gas (in case producer gas is being used). The gas and air meet at the base of the retort, burn, pass up the heating flue, over the top, down the other side, and into the checkerwork. Each retort is heated separately to allow better control of the temperature. When the checkerwork has cooled, the current is reversed, the gas and air passing through the checkerwork, which has meanwhile been brought up to heat. If coke-oven gas is used, it is not preheated (owing to the danger of decomposition) but is introduced through nozzles into the heating flues. The gas from the retort is taken off at the top through a large main to the condensation and refining plant, where the tar, ammonium sulphate, benzol, etc. are recovered. The gases of combustion are led away through flues *s* and discharged. The products of distillation and refining are indicated in Table IX on page 44.

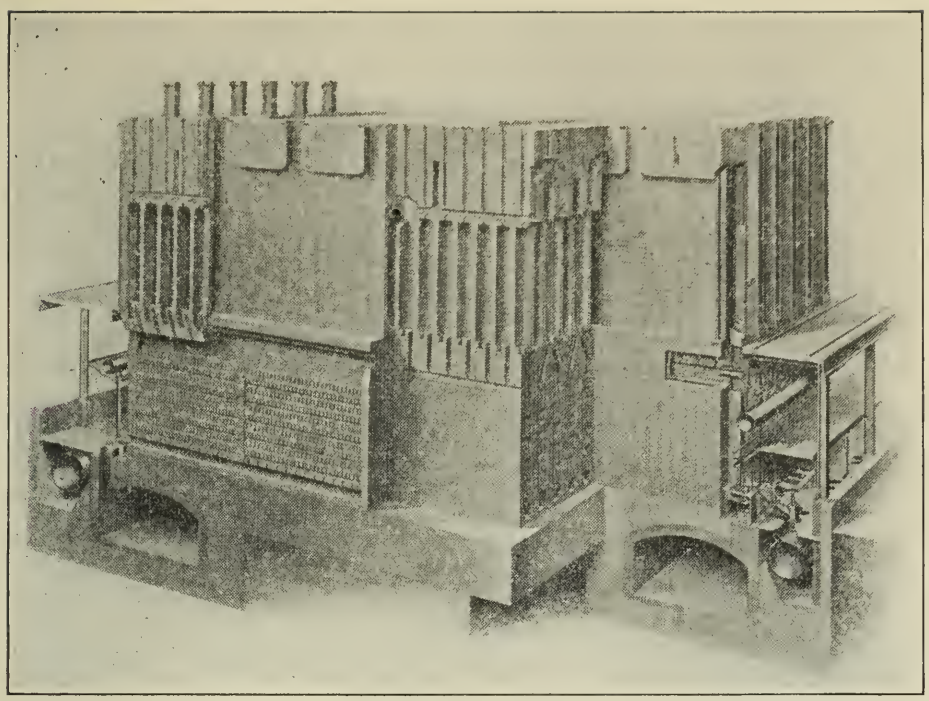

FIG. 10. Perspective view of Becker-coke oven

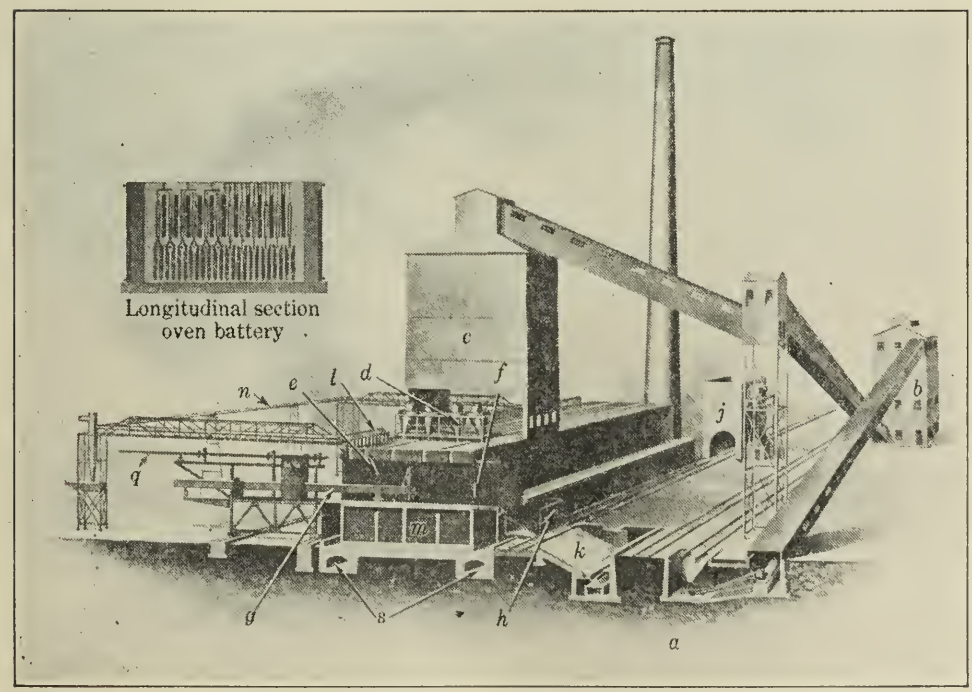

FIG. 11. Perspective view of Becker-coke-oven plant

TABLE IX. PRODUCTS FROM RETORTING ONE TON OF BITUMINOUS COAL

Gas	12,000 cubic feet
Ammonium sulphate	7.25 pounds
Benzene	10.20 pounds
Toluene	3.00 pounds
Xylene	1.50 pounds
Phenol	0.50 pounds
Naphthalene	0.34 pounds
Anthracene	0.25 pounds
Pitch	80.00 pounds
Coke	1350.00 pounds

The coal, crushed to 2 inches or smaller in size, is charged into the furnace through holes in the top by means of hoppers *d*. A

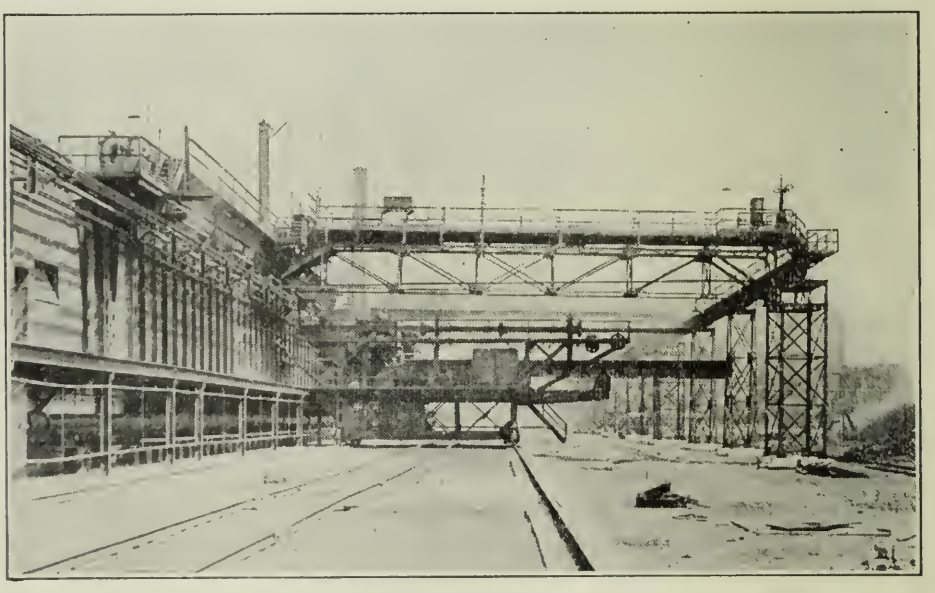

FIG. 12. Side view of pushing machine

reciprocating leveling bar *q*, on the pushing machine, is inserted through a hole in the retort door and levels off the charge, which comes to within about 10 inches of the top of the retort. The doors of the oven are firmly bolted into place and sealed by means of a clay mixture. When the coking is complete the retort is discharged by means of the pushing machine. This consists of a heavy bar *g*, to the end of which is attached a ram just a little smaller than the cross section of the retort. (Such a pushing machine is shown in Fig. 12.) The coke is received in the car *h* and taken to the quenching tower *j*, where it is cooled with water and then spread out on the

coke wharf *k* to be taken to the storage pile when desired. Recently systems of internal quenching (to conserve the heat of the steam) have been developed.

67. Semet-Solvay retort. This differs from the Koppers oven chiefly in the method of heating the retorts. Fig. 13 gives a

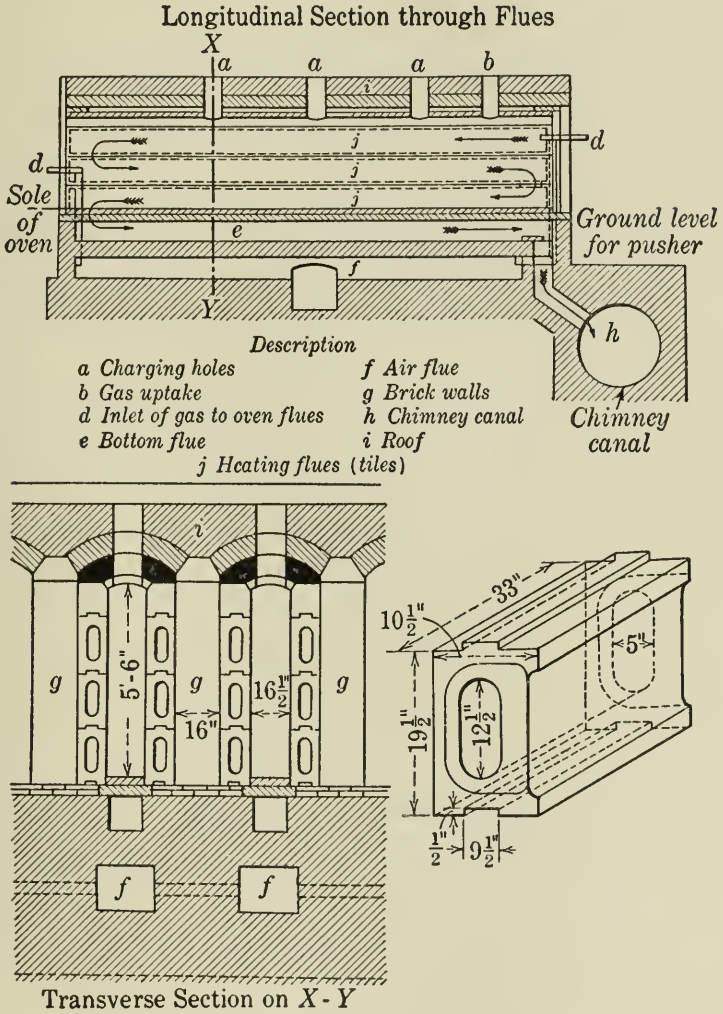

FIG. 13. Semet-Solvay retort

longitudinal and transverse section as well as a perspective view of one of the special tiles. Gas enters the flue at *d*, meets preheated air at 250° C., and burns. The products of combustion pass down through the furnace as indicated by the arrows to the bottom heating flue *e*, and thence to the common chimney *h*. Three charging pipes, *a*, and a gas uptake pipe, *b*, are indicated in the upper part of the retort. The regenerative system is much the same as in the Koppers retort.

68. The beehive versus the retort. In Europe retorts have completely replaced the old beehive, but in this country, where large sums of money are invested in the latter type, it will be some time before they go out of use. The progress that retorts have made during and since the World War is very encouraging. It is an economic crime to coke coal in a beehive, owing to the loss of tars and gases. The beehive is suited only to certain coals. While the beehive plant is much cheaper than a retort plant, the yield of coke is smaller. On the other hand, retort ovens are suited to a great variety of coals. The plant is more expensive than that of the beehive, but the yield is higher. The total cost of coking is likely to be less than in the beehive if all the volatile matter is burned in the flues, and very much lower if the by-products are recovered. Retort coke is more uniform in size and harder than beehive coke.

69. Liquid fuels in general. Petroleum is the leading natural liquid metallurgical fuel and is meeting with increasing favor every day in this industry. At the present time, in many districts it is cheaper than coal; but even when it is slightly more expensive many operators prefer to use it, since combustion is more nearly perfect and regulation much more easy than with solid fuels. The artificial oils obtained from the distillation of coal or oil shale, or from the iron-blast-furnace gases, are of secondary importance. For the same fuel value the weight and volume of oil is from 60 to 70 per cent of that of good bituminous coal. There is no ash and consequently little dirt. The starting, stopping, and regulation of the fire are much more easily managed. Almost the only disadvantages are odor, loss by evaporation, and danger of explosion and fire. The advantages far outweigh the disadvantages.

70. Petroleum. Crude petroleum is a fluid ranging in color from pale yellow to black. It may be almost as mobile as kerosene or as viscous as thick lubricating oil. The specific gravity is usually given in degrees Baumé. American oils, on the whole, have a lower specific gravity than foreign oils, and range from 47° to 25° Bé. Light-colored oils usually have a low specific gravity. In general, the higher the specific gravity or the lower the degree Bé., the more viscous the oil and the lower the calorific power. The following table gives the ultimate analyses and calorific power of some of our common grades of petroleum:

Source	C	H	O and N	S	Calorific Power (in Calories)
Pennsylvania (heavy) (28° Bé.)	84.7	13.7	1.4	—	10,672
Pennsylvania (light) (39° Bé.)	82.0	14.8	3.2	—	9,963
Beaumont, Texas (22° Bé.) .	84.6	10.9	2.9	1.6	10,578
California (15° Bé.)	81.5	10.0	6.9	0.6	10,360
West Virginia (heavy) (30° Bé.)	83.5	13.3	3.2	—	10,100

71. Prepared liquid fuels. The products of the fractional distillation of petroleum are roughly as follows: the light oils which distill at 150° C. or less; the illuminating oils which distill at from 150° to 300° C.; the coke which remains behind after distillation is complete. The light oils may be further fractionated into petroleum ether (40°–70° C.) and the naphthas (80°–150° C.). These prepared oils have little or no use in metallurgy or as a fuel in industry in general. They are used chiefly as solvents of resins, oils, and greases, as fuel in internal-combustion engines, and for other special purposes.

72. Gaseous fuels in general. Gaseous fuels, in the form of producer gas, coal gas, or water gas, are becoming more and more important every day. This has come about largely because gaseous fuels have many important advantages over solid or even liquid fuels. These advantages are as follows: (1) There is more nearly perfect mixing of the fuel and the air, and consequently perfect combustion can be obtained with but little excess of air over the theoretical quantity required. (2) Since there is a smaller volume of waste products to draw off the heat, a higher temperature can be obtained. (3) Both the air and the gas can be preheated with the waste heat of the furnace, and this not only economizes the fuel but makes possible a much higher temperature. (4) The regulation and control of gaseous fuel make possible much more uniform operating conditions, and, moreover, the furnace responds much more quickly to such changes. (5) The gas need not be produced where it is consumed, since it is easily piped long distances at small cost. (6) In the manufacture of artificial gaseous fuels it is possible to make use of inferior grades of coal, particularly if the gas plant is situated near the mouth of the mine. (7) Gas engines are much more efficient than steam engines, and with them power can be generated more efficiently and more cheaply. In metallurgical plants the principal uses of gaseous fuels (aside

from power purposes) are for open-hearth furnaces, soaking pits, heat-treating furnaces, zinc-retort furnaces, copper-refining furnaces, etc. The leading gaseous fuels are natural gas, coal gas, producer gas, iron-blast-furnace gas, water gas, and oil gas. Their properties and analyses are given in Table X.

TABLE X. COMPOSITION OF GASEOUS FUELS (EXPRESSED IN PER CENTS)*

	C_2H_4	CH_4	H	CO	CO_2	N	O	H_2S	HEAT VALUE IN CALORIES PER CUBIC METER
Natural gas	0.4	93.0	2.0	0.6	0.3	3.0	0.5	0.2	8120
Oil gas	16.5	48.0	32.0	—	—	3.0	0.5	—	7337
Coal gas (illuminating)	5.0	40.0	46.0	6.0	0.5	2.0	0.5	—	5333
Coke-oven gas . . .	1.5	36.0	54.0	6.5	1.0	—	—	0.5	5103
Water gas	—	2.0	45.5	45.5	4.5	2.0	0.5	—	2738
Producer gas	0.4	2.5	12.0	27.0	2.5	56.2	0.3	—	1402
Iron-blast-furnace gas	—	2.0	2.0	24.0	12.0	60.0	—	—	959

73. Natural gas. This was, of course, the first gaseous fuel to be used, but our reserves of this have become so depleted that it is no longer a common metallurgical fuel except in a few favored districts.

74. Coal gas and by-product-coke-oven gas. These gases are produced by the distillation of bituminous coal in retorts, as has been outlined under the process of coking. One net ton of gas coal yields about 10,000 cubic feet of gas. They have a heating power of about 5000 calories per cubic meter. On account of the cost of production they are too expensive to be used as metallurgical fuels.

75. Producer gas. Producer gas is our most important gaseous fuel. It is the result of the imperfect combustion of carbon in air. Experiments have shown that when C is heated in air it begins to oxidize at 400° C., and at that temperature burns mainly to CO_2. The rate of formation of CO_2 increases with the temperature up to 700° C., while the rate of formation of CO increases up to 995° C. Above a temperature of 995° C. no more CO_2 is formed. It follows, then, that a producer run on carbon above 1000° C. ought to furnish a mixture made up, by

* H. O. Hofman, General Metallurgy.

volume, of 34.52 per cent CO and 64.63 per cent N (by weight, 34.35 per cent CO and 64.39 per cent N).

This is not possible in practice, for the producers are not always run at a temperature above 1000° C., and some oxygen passes through the producer and burns the CO to CO_2. Producer gas is usually made from bituminous coal, although it can be made from wood, peat, brown coal, and lignite. Producer gas will contain, by volume,

	Per Cent
Hydrocarbons	3–5
Carbon monoxide	20–25
Nitrogen	55–60
Carbon dioxide	2–8

Nitrogen and carbon dioxide produce no heat; in fact, they are worse than useless, for they carry off valuable heat as they pass up the chimney.

The volume of producer gas obtained from a ton of coal will be about 150,000 to 170,000 cubic feet, having a calorific power of from 33 to 36 calories per cubic foot, or from 130 to 145 B.T.U. per cubic foot.

76. Gas-producers in general. Gas-producers are manufactured in a score of different types. They are classified according to whether they are mechanically raked or hand-raked, whether they have a deep or a shallow bed, and whether they give simple gas, from the combustion of carbonaceous fuel, or mixed gas, from the decomposition of steam injected into the combustion chamber. We will consider two types only: a hand-raked producer making simple gas and a mechanically raked producer giving a mixed gas.

77. The simple producer. This type is well illustrated by the Morgan continuous gas-producer shown in Fig. 14. Such producers are used mostly in small plants whose capacity does not warrant the larger investment called for in the mechanical type. Such producers can use any sort of carbonaceous fuel that will ignite and burn, but they are usually run on either anthracite or bituminous coal. As indicated in the sketch, they consist of a central combustion chamber filled with the fuel. This chamber must, of course, be lined with some refractory material to prevent damage to the steel shell. The fuel is fed in through a charging device consisting of a stationary hopper *a*, carrying

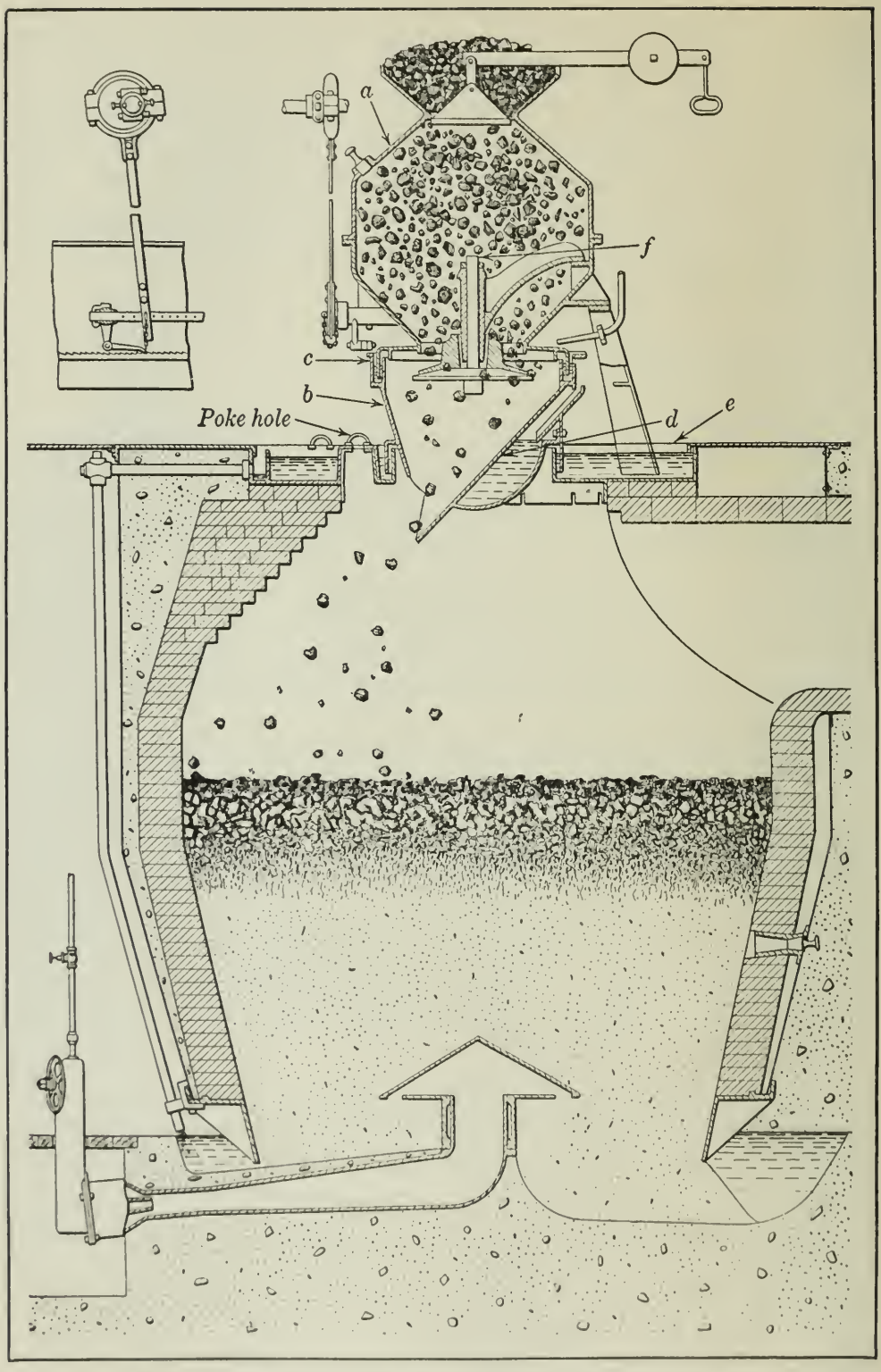

FIG. 14. Section of Morgan continuous gas-producer

at its lower edge a ring *c*, which is water-sealed at the top of the revolving coal-feeding drum *b*, which, in turn, is sealed at the top of the water-cooled producer top plate *e*. The coal-feeding drum *b* is revolved by means of a pawl and ratchet and is suspended from the hopper *a* by means of a shaft *f*. At its lower end it is provided with an inclined water-cooled spout designed to distribute the feed evenly over the bed. Spaced at intervals around the periphery of the top are small "poke holes" through which the top of the charge can be leveled and raked. The air is forced in through the bottom either by natural draft or by a fan. Gas is taken off through the gas main shown at one side, and the ashes are withdrawn from the bottom. In such a producer, holes form in the top of the fuel bed and allow unconsumed air to escape and lower the calorific value of the gas. To overcome this the charge must be raked at frequent intervals through these poke holes. The gas issues from the furnace at a temperature of from 350° to 1000° C., according to whether the producer is being run with a hot top or a cool one. In a producer of this type each pound of coal will produce about 60 cubic feet of gas having a calorific value of about 82 calories per cubic foot.

78. Mechanical gas-producer. The Wellman producer (Fig. 15) is a good example of an American mechanical producer with a revolving bed. The top *a* of the producer is stationary, while the body *b*, together with the grate, revolves. The top of the producer is water-cooled and provided with a gas outlet *l*, a mechanical feed *m*, a poker *c*, and a series of hand poke holes. A water seal prevents gas from escaping at the contact between the top and the body. The poker *c* makes an oscillating motion driven by the mechanism at the right. The producer body is provided with a cast-iron ring *d* at its lower end, serving to seal the body in the ash pan, which is kept full of water. The ring *d* also serves to support the body by means of a three-armed spider *e*. Air is fed both through the center tuyère and through openings in the spider arms near the body walls. Steam can also be injected in this manner. The ash pan *f* rests on six rollers *g*, which are in turn supported by the foundations. The ash pan is revolved by means of the spur gear *h* and the driving mechanism *i*. The ashes are discharged by means of a stationary plow *k*, which can be pushed into the water seal to remove the ashes or withdrawn from it when not in use.

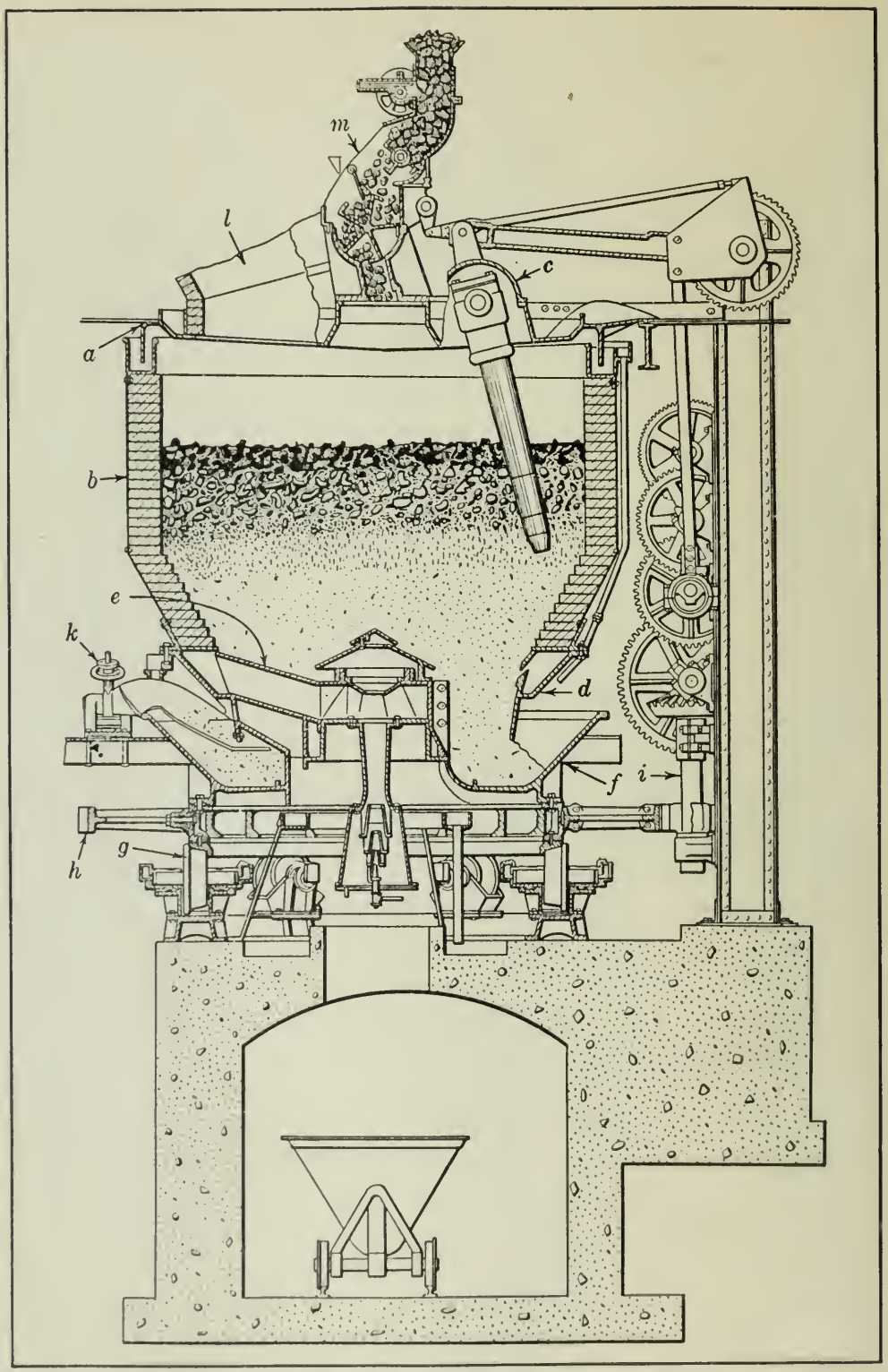

FIG. 15. Wellman mechanical gas-producer

The water-cooled poker *c* is suspended from bearings on the top cover and caused to swing from center to edge of the fuel bed in a nearly vertical plane. The simultaneous motion of the poker and the fuel bed causes the poker to describe a series of loops as indicated in Fig. 16. A producer of this description, 10 feet in diameter, will gasify about 1.5 tons of bituminous coal per hour, with a power consumption of 3 horse power and a water consumption of 1200 gallons per hour.

When in operation the producer has three zones: the lower one of hot ashes, a middle one of glowing carbon, and an upper one maintained at a considerably lower temperature (depending upon whether or not the furnace is being operated with a hot top). A mixture of steam and air is injected through the tuyères and becomes preheated in rising through the hot ashes. Coming in contact with the red-hot carbon, the water is dissociated into O and H, while part of the carbon of the charge burns to CO_2. In passing up through the fuel bed this CO_2 is reduced by the carbon to CO, while a part of the hydrogen unites with the carbon to form hydrocarbons like methane. In the upper zone the temperature is always much lower, but there is sufficient heat there to liberate the rich hydrocarbons found in the bituminous coal.

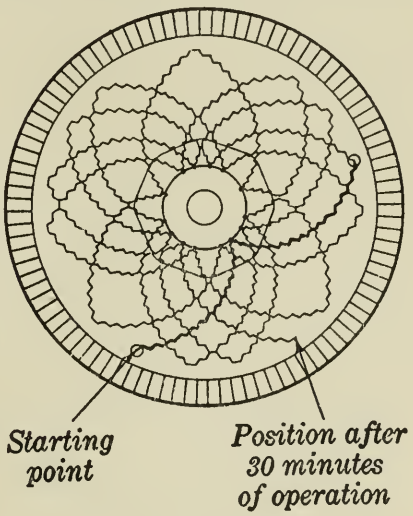

FIG. 16. Poker path

A certain amount of CO_2 is always formed, even in the best practice. In fact, it is inevitable, but if kept within proper limits it does not constitute a net loss of efficiency. The loss increases rapidly above 4 per cent CO_2, however, even when the gas is carried hot in short flues. If the gas is too hot, the hydrocarbons are broken up and deposit their carbon as soot. If the gas is too cool, the result is equally bad, for the low gas temperature permits the deposition of tar in the flues. The most economical results are obtained with a CO_2 content of about 4 per cent, with a gas temperature ranging from 600° to 650° C. and with flues less than 100 feet in length.

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CHAPTER IV

ROASTING

79. General. Roasting may be defined as heating to an elevated temperature, without fusion, or at most with incipient fusion, a metal or metallic compound in contact with oxygen, water vapor, carbon, sulphur, or chlorine, in order to effect a chemical change and to eliminate a component by volatilization. Ordinarily we distinguish the following: calcination, drying, sulphatizing roast, oxidizing roast, chloridizing roast, and nodulizing. While not strictly within the province of roasting, calcination and drying are best treated in this chapter.

80. Drying. Drying is not ordinarily carried out as a separate operation in the smelting of ores; but where excessive moisture might interfere with or seriously retard any subsequent treatment, the ore may be subjected to a preliminary drying operation to remove this. Ores with less than 5 per cent of moisture can be treated directly unless they are being crushed dry or treated by a chloridizing operation. The concentrates from milling operations (often carrying from 10 to 25 per cent of moisture) must be dried before they are roasted. The simplest method for the removal of water from ores or concentrates is that of air drying. The material to be dried is spread out on a floor of brick or sheet metal, heated by a fire or by hot air, and stirred from time to time either by hand or with mechanical rakes. Such methods, adequate for small plants, are not applicable to large ones, owing to the high cost of labor. The Lowden drier, a horizontal-hearth furnace, along which the ore is moved by a flight conveyor, will reduce the moisture to less than 1 per cent. Another method is to use a revolving kiln similar in construction to the cement kiln. This is set at a slight pitch, the ore traveling in one direction and the heated air in the other. In the Ebro drier, shown in Fig. 17, the cylinder is heated by an outside fire box, so that the products of combustion do not come in contact with the ore. While both these

types are efficient driers, they have the disadvantage of producing a considerable amount of fine dust (flue dust) by the attrition of the particles as they tumble over and over in their passage along the hearth. The amount of water absorbed by the air current rises very quickly with the temperature, so that if the drying is to be at all efficient it must be carried out at as high a temperature as possible without fusing, or sintering, the material under treatment. Intimate contact between the ore and the air is necessary, and this is favored by a small size of ore (not larger than 2 inches in diameter) and by frequent stirring.

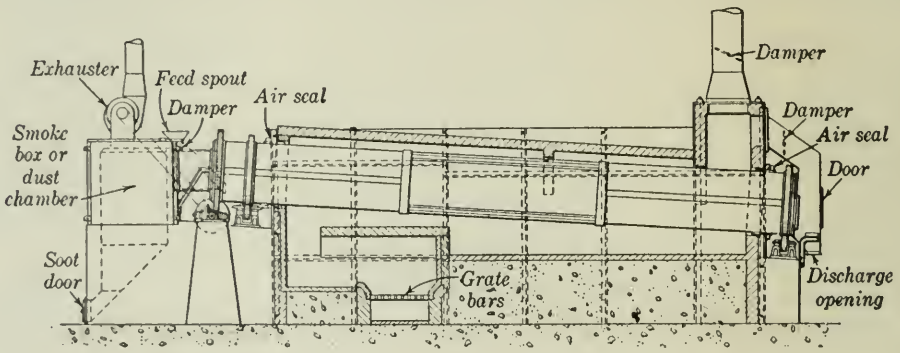

FIG. 17. Section of an Ebro-type drier

81. Calcination. In calcination the aim is the elimination of some component at a temperature below the fusion point without otherwise chemically affecting the resulting product. Calcining is confined mainly to the driving off of the chemically combined water from oxide and carbonate ores and clays, and to the burning of limestone, dolomite, and magnesite. It differs from drying only in the higher temperature used. The apparatus and mode of treatment are much the same as those employed in drying. One exception might be noted; that is, the use of shaft furnaces in burning carbonates. Most of the hydrated substances encountered in metallurgy give up their water below 300° C.; carbonates require from 600° to 800° C.; sulphates and clayey substances, from 600° to 1000° C.

82. Oxidizing roast. An oxidizing roast is usually carried out for the purpose of eliminating the S, As, Sb, or Te. These elements often seriously interfere with the carrying out of subsequent metallurgical operations. In general, if we heat powdered metallic sulphide in contact with air to its *ignition point*, or that temperature at which the affinity of the sulphur for

oxygen becomes greater than for the metal, there is formed the metallic oxide and sulphur dioxide, thus:

$$MS + 3\,O = MO + SO_2 + \text{calories.}$$

The SO_2 that is formed may pass off unchanged or by catalysis in the presence of air be converted (in part at least) into SO_3, thus:

$$2\,SO_2 + 3\,O_2 + SiO_2 = 2\,SO_3 + 2\,O_2 + 22{,}600 \text{ calories.}$$

In the absence of air the conversion may be as follows:

$$3\,SO_2 = 2\,SO_3 + S.$$

The ignition temperatures of minerals vary between wide limits. The roasting of pyrite is relatively easy, while zinc blende is rather difficult to roast. In Table XI are given the ignition temperatures (at which the first SO_2 is given off) of some of the more common metallic sulphides.

TABLE XI. IGNITION TEMPERATURE OF SULPHIDES (IN DEGREES CENTIGRADE)

MATERIAL	GRAIN 1 MILLIMETER IN SIZE	GRAIN 1–2 MILLIMETERS IN SIZE	GRAIN OVER 2 MILLIMETERS IN SIZE
Pyrite	325	405	472
Pyrrhotite	430	525	590
Stibnite	290	—	340
Chalcocite	430	—	679
Sphalerite	647	—	810
Galena	554	—	847

Roasting is a slow operation and must be carried on at a low temperature; otherwise sintering, or fusion, of the ore results, and this will retard or even entirely stop the operation. The ore must be stirred frequently in order to bring fresh surfaces in contact with the air, and heated gradually until at the end of the operation a temperature is reached sufficient to decompose any sulphates that may be formed. In connection with the formation of sulphates it should be noted that an ore may purposely be given an incomplete roast, so that the sulphur remaining behind is in the form of both sulphide and sulphate. On the other hand, it may be given a "dead," or "sweet," roast when all the sulphur, or as much of it as is economically possible, has been expelled. Sometimes

steam is injected in an oxidizing roast; but it is expensive, and its oxidizing effect is debatable.

As an example of a typical oxidizing roast we will take the roasting of a pyritic ore and follow the reactions which occur when it is slowly heated in contact with air. Combustion of the sulphur starts at a temperature of about 350° C. (depending upon the size). The pyrite is decomposed, and the atom of sulphur given off is burned to SO_2, thus:

$$FeS_2 + O_2 = FeS + SO_2.$$

As the temperature increases, the FeS thus formed begins to oxidize, thus:

$$FeS + 3\,O = FeO + SO_2.$$

This is an exothermic reaction and yields 113,600 calories.

Under certain conditions, as in the presence of a catalyst or a large excess of air, the FeS first formed may go over into a mixture of oxide and sulphate, thus:

$$3\,FeS + 11\,O = 2\,SO_2 + Fe_2O_3 + FeSO_4.$$

The ferric sulphate may be decomposed by heat, thus:

$$FeSO_4 = FeO + SO_3.$$

This reaction is endothermic and takes place only in the hotter part of the furnace.

83. Roasting apparatus in general. The character of the ore to be treated, the kind of roast required, the tonnage to be handled, and the cost of installation and operation have resulted in a great diversity of form in the apparatus for roasting ores and metallurgical products. For our purposes this apparatus can be divided into five classes: (1) heaps; (2) reverberatory furnaces; (3) mechanically raked furnaces; (4) kilns; (5) blast-roasting apparatus.

84. Heap roasting. While this is a simple process, the increasing cost of labor and the necessity of investing large sums of money in ore have caused it to be generally abandoned. It requires that the ore be in lump form, although lump ore may be replaced by briquettes. It consists in piling up the ore in the form of a truncated pyramid upon a foundation of wood and then igniting the ore by means of this wood. Once started (provided the ore contains enough sulphur), roasting will proceed without the application of external heat.

The building of the heap is of the utmost importance, for an

improperly constructed heap will develop hot spots or give an imperfect roast. The height is usually about 6 feet. This height will vary inversely as the percentage of sulphur, for a high heap develops a stronger draft, and consequently a more intense oxidation, than a low one. An ore with only 10 per cent of sulphur may be 7 feet in height, while a rich ore with 35 per cent of sulphur may be less than 5 feet. The length and width have little effect on the results of the roast; they are simply matters of convenience for the operator. It is rather hard to give figures for time and the elimination of sulphur, for naturally these will vary between wide limits. An average may be set down as three weeks for the roasting operation and about 7 per cent of sulphur remaining behind in the product.

The ground upon which the heaps are built must be firm and impervious to water, for many of the roasted products contain copper. Unless some provision is made for saving it, this copper will be leached out and lost as the rain falls upon the heap. Heap roasting is usually practiced in connection with low-grade copper ores such as occur at Rio Tinto in Spain and at Sudbury, Ontario. The advantages of the process are small consumption of fuel and cheapness of installation and operation. In most localities the disadvantages more than outweigh the advantages, for the ore must be coarse, the elimination of sulphur is incomplete, a great deal of capital is tied up in the large tonnage of ore being treated, there is loss through dusting and leaching, and the gas from the oxidation of the ore kills all vegetation in the neighborhood and frequently involves the company in expensive lawsuits.

85. Hand-raked reverberatory furnaces. While hand-raked furnaces have been largely displaced by mechanical furnaces today, we do find them from time to time in metallurgical plants that treat high-grade products or work on special processes. They may be classed as intermittent or continuous. In the former, cold ore is charged, roasted, and withdrawn. It is obvious that this method is very wasteful of heat and labor and can be used only on high-grade material. In the continuous furnace the material passes through the furnace without interruption.

A typical hand-raked reverberatory is shown in Fig. 18. It consists of a furnace with a flat hearth and an arched roof. The fuel is burned at the fire box located at one end, and the flame and heat from the combustion are reflected by the roof down

onto the ore as it lies upon the hearth. The products of roasting, along with the gases of combustion and the flue dust, are taken off through a flue at the opposite end. Such a furnace has a hearth from 40 to 80 feet (usually 60 feet) long and from 8 to 17 feet wide, the width being limited by the ability of the operator to stir, or rabble, the ore effectually. The hearth is commonly divided into three or four steps, with a drop of about 3 inches between steps to facilitate the passage of the ore through the furnace. Each of these hearths is served by two working doors

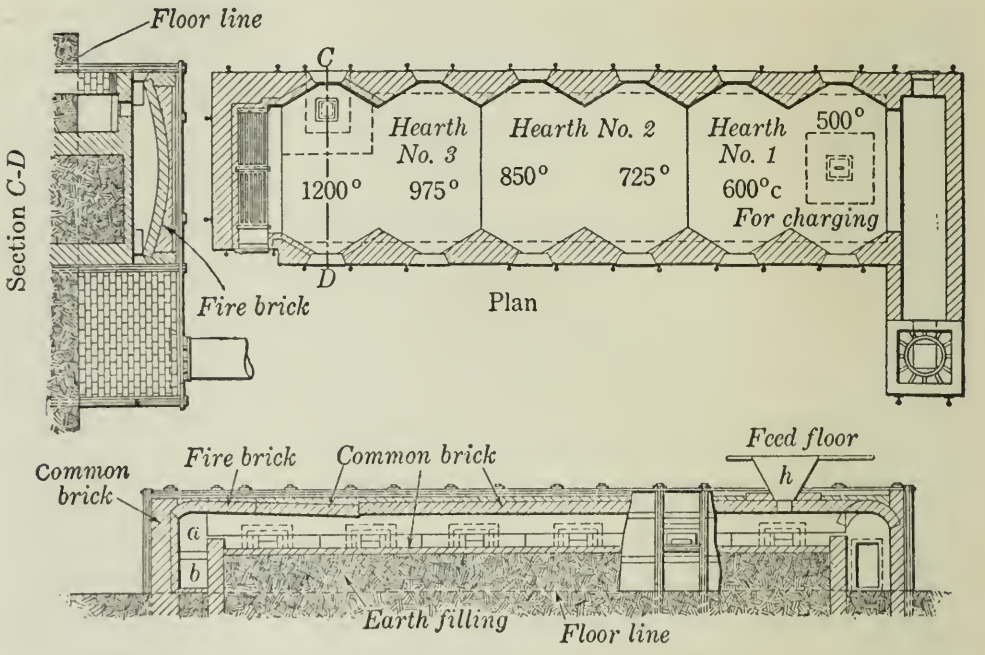

FIG. 18. Hand-raked reverberatory furnace

on each side of the furnace. The furnace is usually built of red brick, except the discharge opening, the fire bridge, and the fire box, which are built of more refractory material to withstand the heat. In operation the charge is dropped through the small opening shown in the roof of the furnace, and one of the operators levels off the ore, as it falls upon the hearth, into a layer from 4 to 8 inches deep, depending upon the character of the material. Air for roasting is admitted through the working doors and sometimes through openings in the fire bridge. This air also serves the purpose of cooling the fire bridge and lengthening the life of the brick. The ore is rabbled and turned over by operators every fifteen or thirty minutes and is gradually worked down the furnace toward the fire-box end, where it is discharged

through a small opening in the hearth of the furnace into a car, or "buggy," on a track below. This working of the ore is accomplished by means of rabbles, paddles, and slice bars. These break up the sintered material as it forms in the furnace when the temperature momentarily becomes too great.

To economize floor space and heat, these furnaces are often built with from two to four superimposed hearths. The ore is fed at one end of the upper hearth, travels along it, as described, to a slot at the other end, through which it drops onto the next hearth and is then moved in the opposite direction. Such furnaces have two distinct disadvantages: (1) when there are three or more hearths it is difficult for the workmen to handle their tools, because the furnace is very high and they are obliged to move from hearth to hearth; (2) many ores corrode or damage the hearth, and repairs to the lower hearths are both difficult and expensive.

86. Mechanically raked furnaces. These have certain advantages over the hand-raked furnaces: (1) they are less expensive to operate; (2) the admission of air can be more closely controlled and the results rendered more uniform and less dependent upon the skill and attention of the operator. On the other hand, they have certain inherent disadvantages: (1) many of the moving parts are exposed to corrosive gases and high temperatures, so that repairs are costly and frequent; (2) they are not suited to sticky ores, for these form balls and lumps which interfere with the mechanism; (3) they are not suited to dead roasting, since such operations are too costly and must often be conducted at high temperatures. In connection with (3) it should be noted that the conditions for dead roasting are very different from those for rough roasting. For the former it is desirable to have the ore pass through the cool part of the furnace rather quickly and remain for a long time in the hot part while the last bit of sulphur is being eliminated; for rough roasting the opposite is desired. These varying rates of travel in the same furnace cannot be brought about mechanically except at a prohibitive cost.

87. The Wethey furnace. This is a single-hearth reverberatory furnace in which the ore is moved along the hearth by simple mechanical rakes. A 10×50 foot furnace is shown in Fig. 19. The *rabble arm*, which reaches completely across the hearth, has blades set at an oblique angle to the long axis of the furnace. The blades on one side of the furnace are

set in an opposite direction to those on the other, so that the pressure due to the movement of the ore may be equalized. The blades on succeeding arms are also set in opposite directions

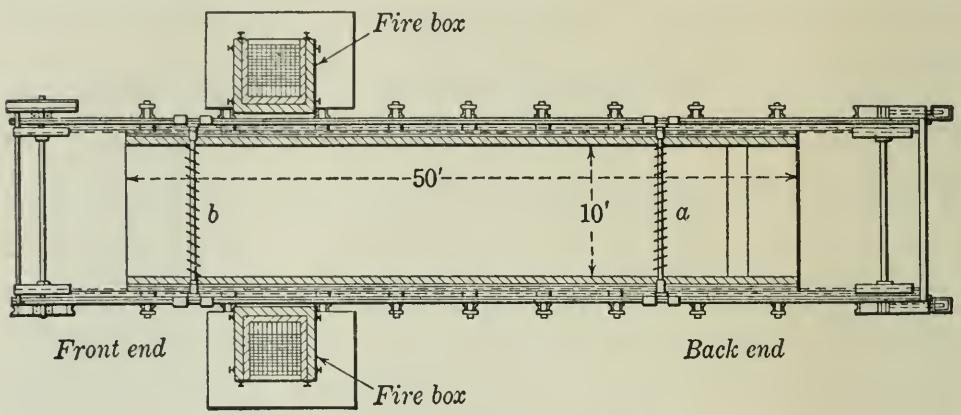

FIG. 19. Wethey furnace

to insure thorough stirring of the ore. The combined effect of the arms as they move through the furnace is to push the ore slowly along the hearth. The rakes are pulled through the furnace by means of chains which pass over pulleys at each end of the furnace. Other furnaces of this type are the Brown, the O'Hara, the Edwards, the Merton, and the Hegeler.

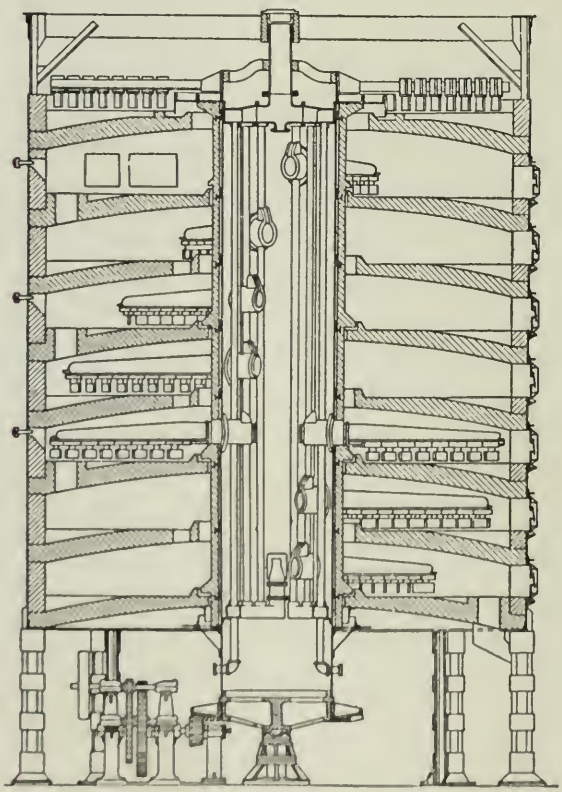

FIG. 20. Modern seven-hearth Wedge furnace (with drier hearth and air-cooled arms)

88. The Wedge furnace. This furnace, of the multiple-hearth type, is one of the most popular in use today in metallurgical plants, particularly for rough roasting on a large scale. It consists of a vertical cylindrical sheet of boiler plate divided into seven hearths as shown in Fig. 20. The furnace is about 14 feet in diameter and 28 feet in height. The hearths, walls, and roof

are lined with brick in order to protect the metal and conserve the heat. There is a central vertical shaft of boiler plate lined on the outside with brick. To this shaft are attached the rabble arms, two to each hearth. These rabble arms, which stir the ore, are cooled by means of air or circulating water (see water launder in Fig. 22). The central shaft is driven through a train of gears beneath the furnace. One distinct advantage of this furnace lies in the fact that the operators may work in this shaft in order to remove and repair the rabble arms. (Such repairs are more difficult in the MacDougall type of furnace, to be described later.) The ore is fed upon the upper hearth, which, being warmed by the heat generated in the roasting operation, serves to dry the material. The ore passes from the outer edge across the upper hearth and falls through a slot upon hearth No. 1. It passes across this hearth to a slot near the periphery and there drops through onto hearth No. 2 and thus in a zigzag fashion through the furnace, and drops finally into a car or onto a conveyor beneath the furnace. The arms make one revolution in about one and one-fourth minutes.

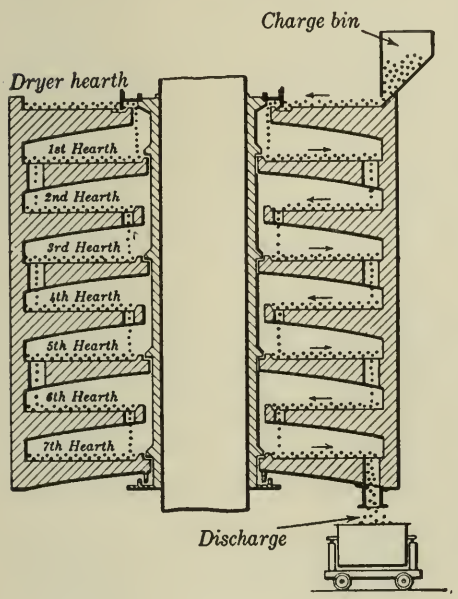

FIG. 21. Path of charge in Wedge furnace

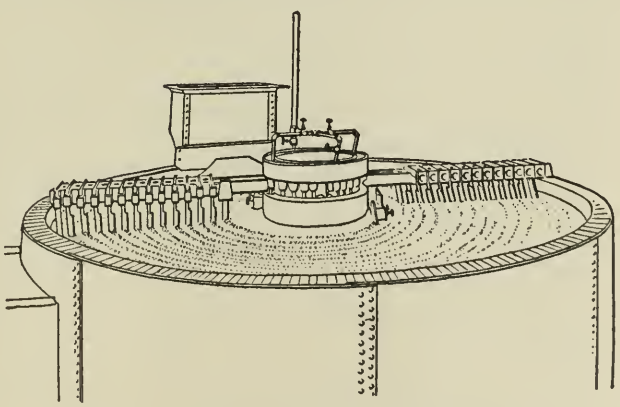

FIG. 22. Wedge drier or preheater top

For most rough roasting, once the ore is ignited, the reaction furnishes enough heat to make the process a continuous one. For ores that are difficult to roast or low in sulphur, an external fireplace may be provided to furnish the

necessary heat for the process. The capacity of the furnace will vary between wide limits, depending upon the character of the mineral, the percentage of sulphur in the original ore and in the calcine, and the number of hearths. The capacity of a furnace 20 feet in diameter roasting pyritic copper ore for matte smelting is about 75 tons per 24 hours. Recently the manufacturers of the Wedge furnace have brought out a new furnace in which the cooling of the rabble arms is accomplished by means of air, as shown in Fig. 20. This furnace does away with the difficulty of leaky arms and rabbles so common in the water-cooled type.

89. The MacDougall furnace. The MacDougall furnace operates on much the same principle as the Wedge, being a multiple-hearth furnace with revolving arms. The chief difference is in the central shaft, which carries the rabble arms. In the MacDougall furnace this consists of a 9-inch hollow steel shaft to which the rabble arms are fastened. Cooling water for the arms is forced down through a 3-inch pipe in this central shaft to a point near the bottom. It returns to the top through the annular space between this 3-inch pipe and the inside of the central shaft and discharges at the top into an annular launder. The furnace is supported and driven in much the same way as the Wedge. A furnace 18 feet in diameter by 18 feet in height has a total hearth area of about 1600 square feet and will treat about 60 tons of sulphide ore per 24 hours, reducing the sulphur content to 7 per cent. Like the Wedge, this furnace makes considerable flue dust as the hot ore drops from hearth to hearth. An average figure for this will be about 4 per cent of the charge. A section of a MacDougall furnace is shown in Fig. 23.

90. The Nichols-Herreshoff furnace. This is a multiple-hearth roasting furnace with air-cooled arms. A seven-hearth type with a drying hearth is shown in Fig. 24. Air is supplied, under a pressure of from 1.5 to 3 ounces per square inch, to the air housing at the base of the shaft. Stuffing boxes serve to make this connection air-tight. A step-bearing carrying the central shaft runs in a bath of oil.

The central shaft is constructed in sections, and the part between the lower hearth and the drying hearth has two compartments. The inner central compartment is called the cold-air tube, and the outer annular compartment the hot-air compart-

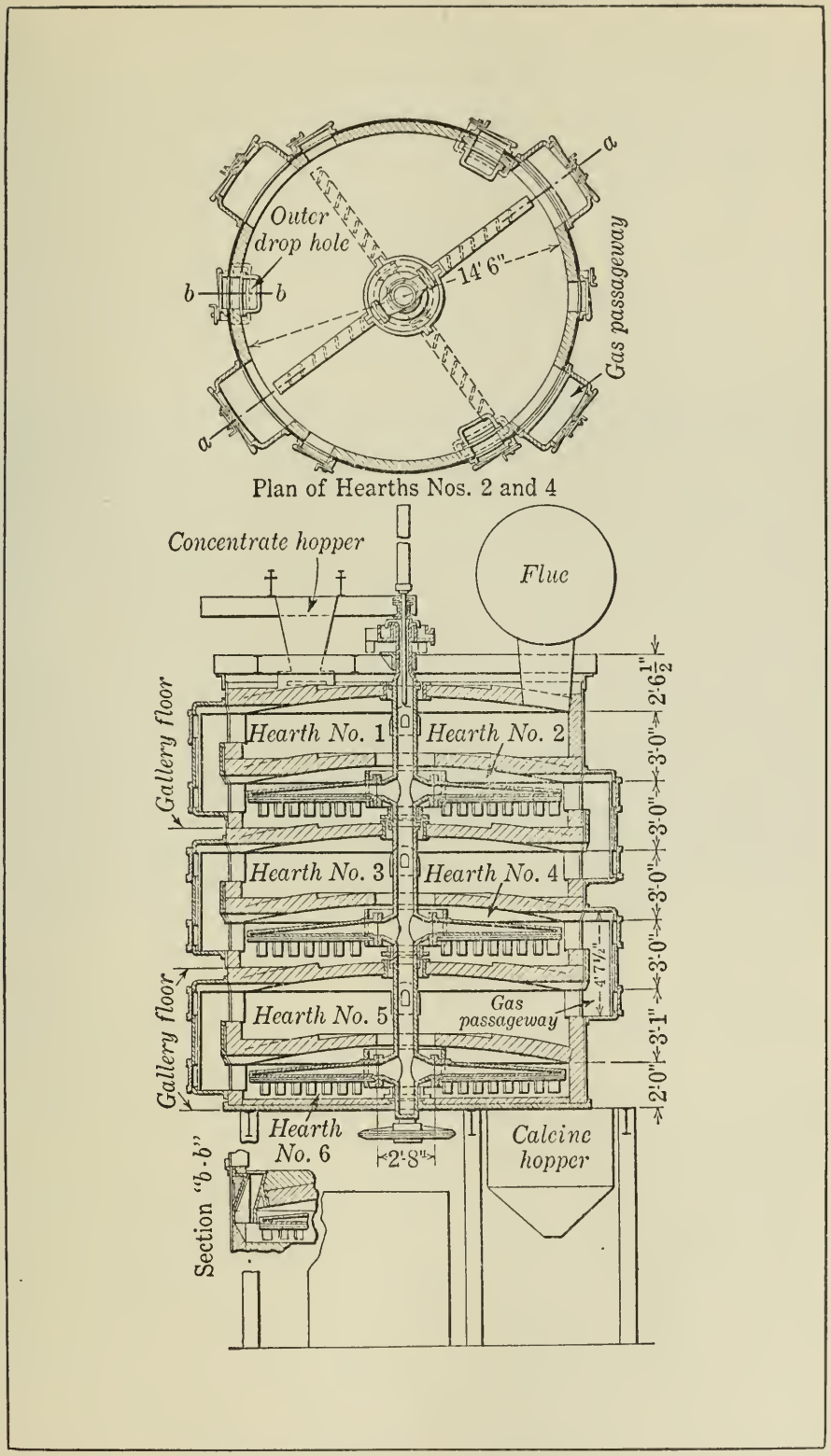

FIG. 23. MacDougall furnace

ment. Two or more rabble arms are attached to the central shaft at each hearth, and each rabble arm has a central tube, or partition, so that the cooling air can be conducted to the extreme end of the arm and back through the outer air space to the shaft, and thence, through openings, into the hot-air compartment. From there it may be discharged, from the top of the furnace, into the air, or, better, used for combustion purposes on the hearths.

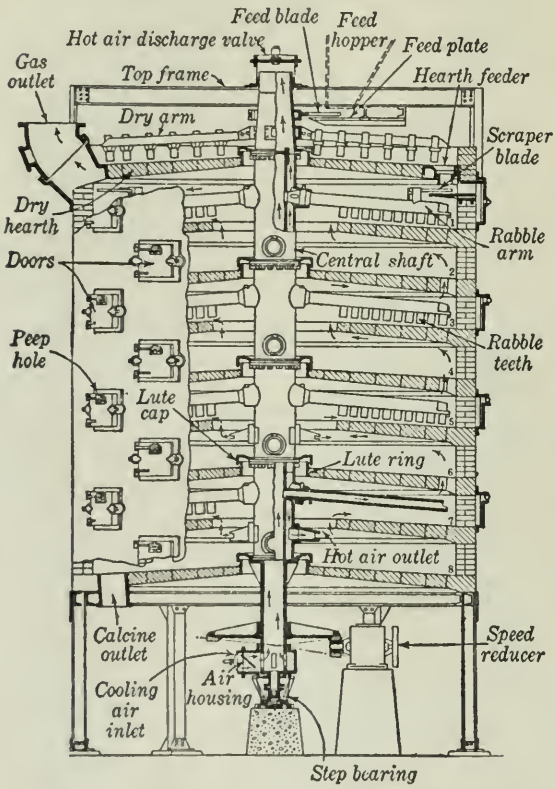

FIG. 24. Nichols-Herreshoff furnace

This hot combustion air, at a temperature of from 200° to 300° C., may be collected from the top of the shaft through a housing and conducted through vertical steel pipes (preferably insulated) to any of the hearths. It may be discharged directly into the furnace from the rabble arms on one or more of the hearths, or it may be discharged into the furnace through hot-air arms attached to the outer wall of the shaft and opening into the hot-air compartment. Any one of these methods will result in a notable conservation of the heat and the roasting will be quicker and more efficient.

The ore is delivered to the feed plate suspended from the upper frame of the furnace. An adjustable cutter, revolving with the central shaft, scrapes off a regulated amount onto the top drying hearth. The rabble arms then move the ore across the hearth to the periphery, where it drops through an opening onto a similar feed plate suspended from the side wall of the furnace just above the first roasting hearth. This effectually seals this opening in the furnace and prevents any air or gas leakage. A cutter mounted on the rabble arm of the first hearth removes the ore from this feed plate. Its course through the furnace is

much the same as in the types of circular multiple-hearth furnace previously described. It is discharged from the bottom hearth through a sealed calcine opening. The rabble arms are of two types: the bolted type, fixed by bolts to the central shaft, and the quick detachable type, held in place by means of a special socket and alloy-steel pin.

91. Kilns. These consist of revolving iron cylinders having a slightly inclined axis and lined wholly or partly with brick. They are used but little for roasting, their field being either

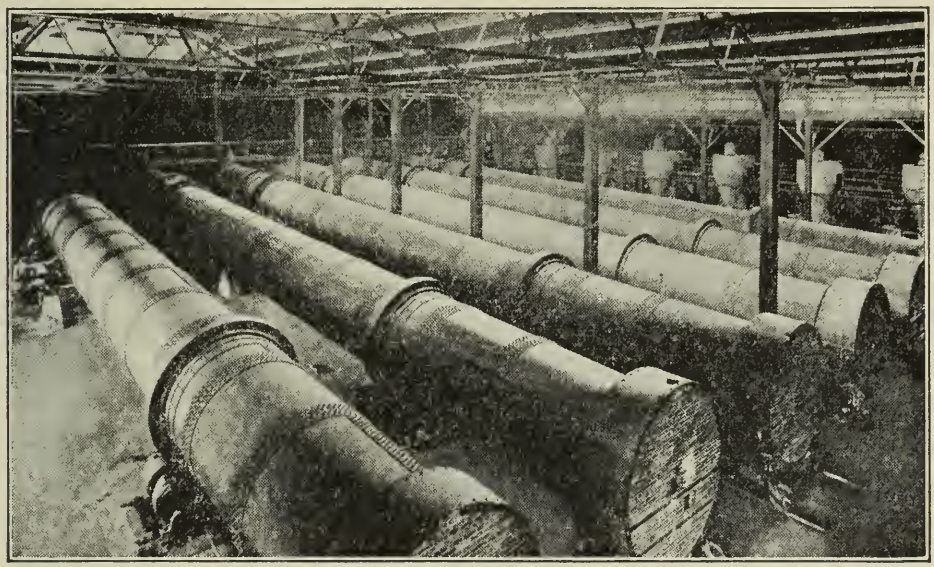

FIG. 25. Kilns

drying, nodulizing, or calcining. The advantages claimed for this type of furnace are that repairs are low and that the ore is stirred continuously and thoroughly. So far as roasting is concerned, however, these advantages are more than offset by the large amount of flue dust formed by alternately raising the ore along the sides and dropping it to the bottom, and by the loss of heat through radiation. Another limitation to their use lies in the fact that with refractory ores the layer of material along the bottom has to be so thin, in order to obtain a good roast, that the furnace is likely to have a very small capacity. The capacity of such a furnace will depend upon the inclination of the axis, the speed of rotation, and the character of the ore. A typical kiln such as is used in the burning of cement or in the calcination of magnesite is shown in Fig. 25. Kilns vary

in size from 6×25 feet up to 9×125 feet. Owing to variations in operating conditions, general figures as to capacity are almost impossible to give.

92. Nodulizing. There has been a notable increase in kiln installations in the past few years, owing to the increasing popularity of *nodulizing*. This consists in bringing the material to a temperature at which incipient fusion begins, and at the same time rotating it in a kiln. The pasty material then tends to form into granules, or nodules, from $\frac{1}{8}$ inch to 6 inches in diameter, depending upon the composition of the ore and the conditions in the furnace. This is a particularly attractive process for the treatment of fine materials which otherwise would be unsuitable as blast-furnace feed (flotation concentrates, for example). The normal operating condition of the kiln is to have the first 60 per cent of the length act as a preheater, the next 30 per cent act as the fusion zone in which the material will begin to ride around with the kiln and form small balls, and the last 10 per cent act as the nodulizing zone where the action is completed. The process has decided disadvantages, chief among them being the large amount of flue dust formed, the cost of fuel, and the formation of accretions, or large balls, that tend to choke the kiln or materially reduce its capacity. The following table shows the character of the work done:

	Flue Dust	Nodules
	Per Cent	*Per Cent*
Through $\frac{1}{2}$ inch on $\frac{1}{4}$-inch mesh	—	54.21
Through $\frac{1}{4}$ inch on $\frac{3}{16}$-inch mesh	—	23.16
Through $\frac{3}{16}$ inch on $\frac{1}{16}$-inch mesh	—	20.60
Through $\frac{1}{16}$ inch on 80 mesh	75.0	1.95
Through 80 mesh	25.0	0.08
Sulphur	11.9	4.95

93. Blast roasting in general. The aim of blast roasting is to roast and agglomerate the finely divided ore by means of forced draft. The apparatus for carrying out this process may be classed as intermittent or continuous, or as down-draft or up-draft. We shall describe only the two most popular forms, the Huntington-Heberlein and the Dwight-Lloyd.

In order to accomplish blast roasting it is necessary that the material contain sufficient sulphur so that, once started, roasting

will go on without the application of extraneous heat; that the material be fine enough to ignite easily and allow a ready access of air; and that the heat generated be sufficient to cause the oxides to combine with the fluxes or gangue and form fusible compounds which will bind together the roasted mass. The latter is particularly important, for by this means a pulverulent product, totally unsuited to blast-furnace reduction, may be transformed into an ideal product (sinter) for such reduction.

This process has entirely replaced the ordinary oxidizing roast, particularly in the treatment of lead ores. It has the following advantages: (1) efficient sintering of the material without a heavy loss through dusting or volatilization; (2) reduction of the cost of the plant and of treatment; (3) oxidation and elimination of the sulphur. There is a further advantage, provided that subsequent treatment includes smelting in the blast furnace: the smelting power of the furnace is increased, owing to the absence of fines and to the increased porosity of the charge.

The great success of blast roasting in the treatment of lead ores led to its application to other phases of metallurgy, — to the treatment of copper ores and concentrates, mattes, speisses, flue dust, and fine iron ore. Of course, with the last two products, agglomeration and sintering are the only objects aimed at, for the materials are already low in sulphur.

94. The Huntington-Heberlein pot. This is typical of blast-roasting apparatus as originally developed, and was in very general use in this country until the invention of the Dwight-Lloyd machine, particularly in plants treating lead ores. The common type of Huntington-Heberlein (or "H and H" pot, as it is termed in metallurgical plants) is shown in Fig. 26. It consists of a heavy cast-iron pot supported on a cement or masonry foundation and carrying a detachable hood and offtake pipe for the disposal of the gases from the roasting operation. The original pots were small, holding not more than a ton of charge; but the pots in common use today

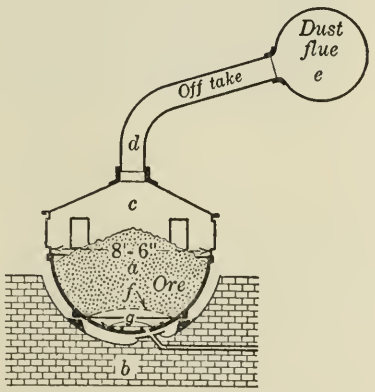

FIG. 26. Huntington-Heberlein pot

are about 9 feet in internal diameter and from 4 to 5 feet in depth, holding from 8 to 12 tons of charge. There is a blast-inlet pipe from 6 to $9\frac{1}{2}$ inches in diameter, which enters at the bottom of the pot. This delivers air under a pressure of from 4 to 16 ounces per square inch to a circular cast-iron plate or grate from 6 to 8 feet in diameter and having about 200 holes, from $\frac{3}{8}$ to $\frac{3}{4}$ inch in diameter, distributed evenly over its surface. At the side of the pot are eyebolts or heavy lugs, so that when the roasting operation is finished the whole pot can be removed by means of a crane and conveyed to the mixing floor, bin, or bedding plant, where it can be discharged by being turned over, and then cleaned and made ready for another charge. The details of the roasting process will be described later, under the chapter on lead.

95. The Dwight-Lloyd (straight line). This machine (shown in Figs. 27 and 28) is of the continuous down-draft type. It consists of a strong frame of structural steel supporting two heavy

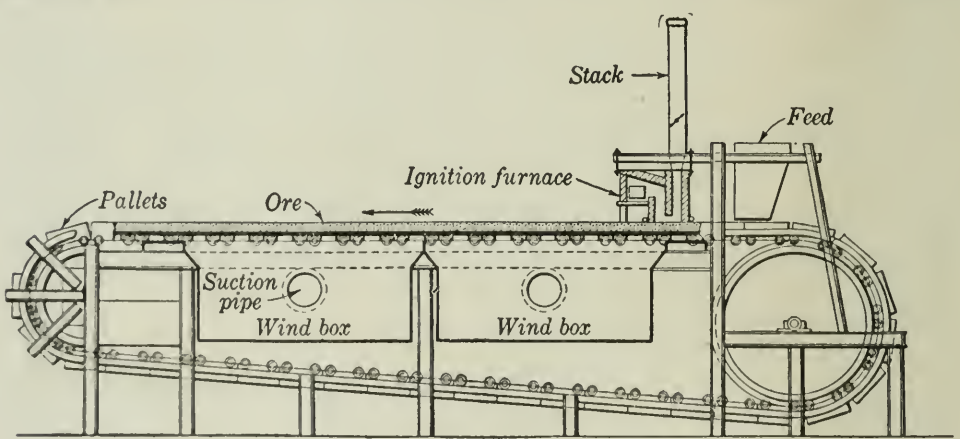

FIG. 27. Dwight-Lloyd continuous sintering machine

sprockets and a steel track, or guide. Traveling on these sprockets and driven by them is an endless system of pallets, or pans, with perforated bottoms. These hold the charge during the roasting process. Underneath the train of pallets is a suction box connected with a fan which induces a down draft through the perforated bottom and through the ore charge. The vacuum in the suction box, governed largely by the character of the charge and the kind of roast desired, will range from 5 to 10 inches of water. Mounted above and near the feed end of the machine is an ignition box for furnishing the heat to start the roast.

Each of the pallets runs on four wheels on the tracks, or guides, except over the suction box, where they pass over a flat plate in order to make a joint that is as nearly air-tight as possible. The whole train is driven by the large sprockets in the direction indicated by the arrow. The pallets are pushed along the track by those that follow. This closes the space

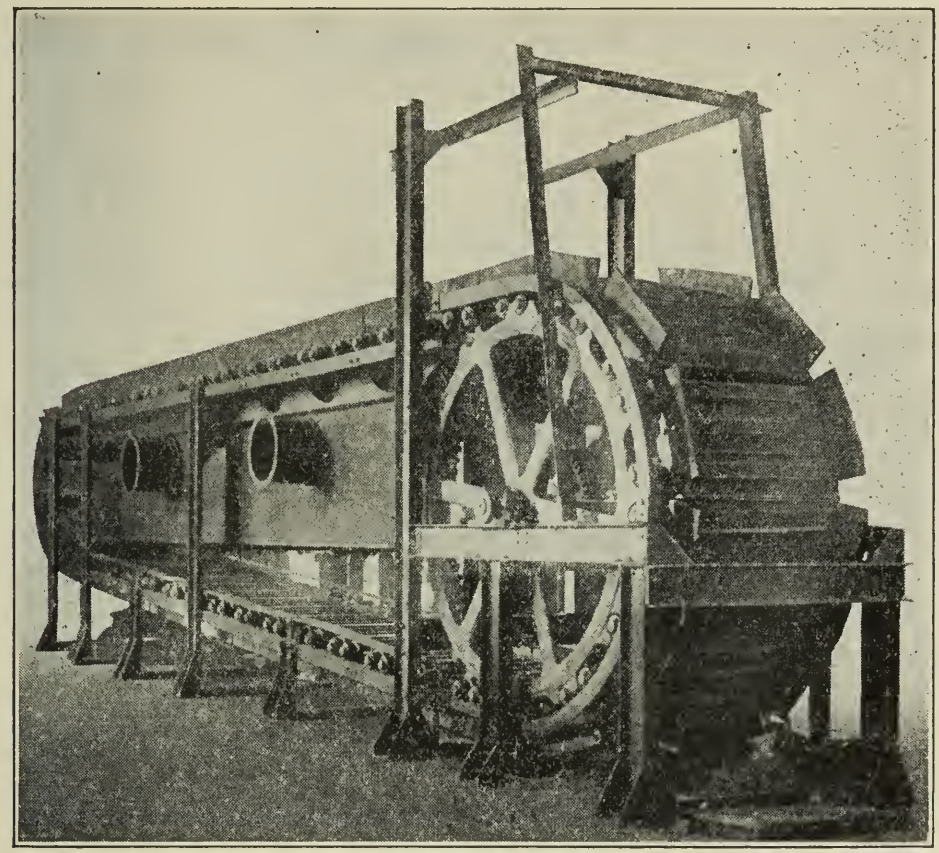

FIG. 28. Dwight-Lloyd machine erected in shop

between the pallets, and a practically air-tight joint is made by the damp, fine ore dropping down into this space. These pallets are made of cast iron, about 42×24 inches, either with straight slots in the bottom or with herringbone grates. When the pallet has passed over the suction box and comes to the curved guides at the end, it slides down these guides and hits the preceding pallet. This jars the sinter cake loose, and it falls into a car waiting below or onto an apron conveyor to be transported to the bins or bedding plant. The force of the blow is determined by the spacing of the pallets.

The cycle of operations is as follows: An oncoming pallet passes under the feed hopper, where it is filled level full (4 inches deep) with a mixture of moistened ore and flux. It next passes under the ignition furnace (either coal-fired or oil-fired), where the top surface of the charge is kindled. Next it passes out over the suction box, where a steady current of air is drawn down through the charge, completely sintering it. The character of the sinter cake and, in turn, the amount of sulphur remaining in it will depend upon the composition of the charge, the strength of the suction, and the rate at which the pallets travel. The cake is discharged as already described, and the pallet returns under the suction box to be loaded again. From time to time it is necessary for the attendant to clean the grates, since they tend to become blinded by fine sintered material. The standard machine now in use is 42 × 264 inches and has two suction boxes 42 inches wide and 11 feet long, but special machines as long as 60 feet are now being used. Each pallet weighs about 800 pounds, and the machine requires from 3 to 4 horse power for its operation. The fans require from 10 to 15 horse power more. The speed of travel of the pallets ranges from 7 to 30 inches per minute, and the tonnage treated, from 50 to over 200 tons per twenty-four hours. The details of the roasting process will be described later under the metallurgy of lead.

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CHAPTER V

SLAGS AND FLUXES

SLAGS

96. Slags and smelting. An ore consists of some valuable metal, such as copper, lead, gold, or nickel, combined with oxygen, sulphur, arsenic, carbon, or some other element and more or less intimately mixed with rock or gangue. The problem before the metallurgist is to separate and recover, in pure form, this small amount of valuable metal from the worthless gangue. This is usually done by the process of smelting, which may be defined as a pyrochemical process, carried on at or above the melting temperature of the compounds, whereby the difference in specific gravity between the fused metal-bearing material, on the one hand, and the fused gangue, on the other, causes them to separate into distinct layers, thus furnishing a basis for a more or less efficient separation. The valuable component is recovered as an impure metal or as a matte (combination of the metals with sulphur). In either case it must be further purified before it can be used in industry. The worthless material from this process is termed a slag and is usually rejected.

It was formerly thought that the slags produced in the reduction and refining of metals were definite chemical compounds, formed in smelting, which retained the same chemical composition in the solid state as they had in the liquid. More extended investigations in recent years have changed this view, and we now believe that slags are in reality igneous solutions of the constituent oxides and of the chemical compounds that may have been formed. For instance, a calcium-iron-aluminum slag is an igneous solution of the oxides of these metals in the silicate. It is obvious that they will show a wide variation in physical character and composition, depending upon the thermal and chemical conditions which prevailed in the furnace at the time

of their formation. Slags ought therefore to follow the laws of solution in a manner similar to that of alloys, and the study of slags shows that within certain limits they do so.

Slags may be classed as silicate and nonsilicate (oxide) slags. The former consist of a mixture of metallic oxides and SiO_2; the latter, of metallic oxides and some acid other than SiO_2 (such as SO_3, P_2O_5, As_2O_3, Sb_2O_5, etc.). Silicate slags are by far the most important in metallurgy.

97. Classification. Many classifications of silicate slags have been suggested, but the only one to be considered in this text is the one depending upon the silicate degree, or the ratio which exists between the oxygen in the base and that in the acid. It is by far the simplest and most common. The following table indicates the different classes:

Name	Oxygen Ratio of Acid to Base	Formula
Subsilicate	$\frac{1}{2}$ to 1	$4\ RO \cdot SiO_2$
Singulosilicate	1 to 1	$2\ RO \cdot SiO_2$
Sesquisilicate	$1\frac{1}{2}$ to 1	$4\ RO \cdot 3\ SiO_2$
Bisilicate	2 to 1	$RO \cdot SiO_2$
Trisilicate	3 to 1	$2\ RO \cdot 3\ SiO_2$

According to the character of the bases, silicate slags may be classed as ferrous or nonferrous. Ferrous slags — those rich in FeO and containing also MnO, CaO, MgO, Al_2O_3, and ZnO with SiO_2 — are produced in the smelting of lead, copper, and similar ores; nonferrous slags — those containing little or no FeO and consisting mainly of CaO, Al_2O_3, MgO, and SiO_2 — are produced in the iron blast furnace. The fusibility in the table above will vary with the proportion of silica, the subsilicate being the most fusible and the trisilicate the most refractory. The silicates with a high percentage of silica are also very viscous, so that the metal-bearing constituents do not easily settle through them. It follows, therefore, that trisilicates are not commonly produced in metallurgical operations. Even bisilicates are uncommon, and most of our slags fall between the subsilicate, on the one hand, and the sesquisilicate, on the other.

Table XII shows the composition of typical slags formed in the smelting of copper, lead, and iron ores.

TABLE XII. COMPOSITION OF TYPICAL SLAGS (EXPRESSED IN PER CENTS)

TYPE	SiO_2	FeO	CaO	Al_2O_3	ZnO	S	MnO	Cu	MgO	P_2O_5
Copper blast furnace .	39.87	22.38	26.83	6.35	1.40	0.52	0.60	0.30	—	—
Copper reverberatory furnace	40.10	34.80	8.50	11.20	2.30	0.70	0.30	0.45	—	—
Lead blast furnace . .	23.0	41.0	15.0	—	16.3	—	—	—	—	—
Lead blast furnace . .	32.0	33.3	21.8	—	4.0	—	1.42	—	1.64	—
Iron blast furnace . .	35.55	—	40.52	12.05	—	—	—	—	8.86	—
Acid Bessemer converter	65.8	18.5	—	—	—	—	11.7	—	—	—
Basic open-hearth furnace	15.1	20.3	42.2	—	—	—	9.0	—	8.5	3.85

98. Fusibility. As already indicated, the fusibility of the slag will depend both upon the silicate degree and upon the character of the bases present. For example, a bisilicate of iron and aluminum might be more fusible than a subsilicate of barium and magnesium, although, in general, bisilicates are less fusible than subsilicates.

99. Specific gravity. This varies mainly with the character of the bases. The extremes are about 5 and 2.5. Certain very basic ferruginous slags may have a specific gravity as high as 5, a common figure for iron-blast-furnace slags is 3, and those formed in lead-smelting are from 3.4 to 3.6.

100. Fluidity. This is a very important property of slags produced in all metallurgical operations, for on it depends the completeness of separation between slag and matte or metal, and, to a large degree, the success of the whole operation. It is obvious that if the slag is to be poured from a crucible or tapped from a blast furnace, it must be more fluid than when raked from a reverberatory furnace or from a basic open-hearth furnace. In order to become fluid most slags must be brought to a temperature of 100° C. or more above their melting point. Viscous slags pass through a more or less pasty stage before they begin to melt or solidify, while fluid slags pass quickly from one state to another.

101. Texture. This depends upon the rate of cooling and the chemical composition. We distinguish vitreous, stony, porcelain, and crystalline slags. Ferrous slags containing Al_2O_3 and those from charcoal iron blast furnaces show a vitreous texture when cooled quickly and a porcelain texture when cooled slowly. Very basic slags rich in alkaline earths have a stony texture.

The following are some of the typical silicates which we encounter as slags in the smelting of copper, lead, gold, silver, and iron ores.

102. Sodium and potassium silicates. These silicates form at relatively low temperatures. Except in fire assaying and in the refining of gold and silver they are of minor importance in metallurgy. They are usually glassy, more or less transparent, and very fluid.

103. Aluminum, calcium, and calcium-magnesium silicates. These three silicates too are of minor importance in metallurgy. Aluminum silicates have a very high formation temperature, and since they are very viscous they are little used. Pure calcium silicates are not often used. Calcium-magnesium silicates are sometimes used in the charcoal iron blast furnaces.

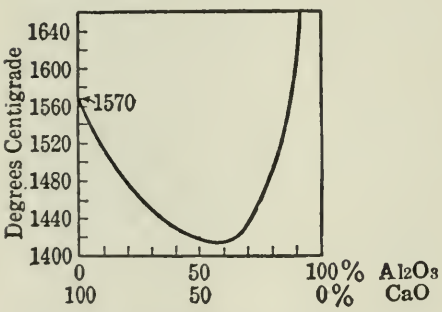

FIG. 29. Formation temperatures of Ca-Al singulosilicates

104. Calcium-aluminum silicates. These silicates are of great importance in metallurgy, for they represent the slags made in the iron blast furnace. Fig. 29 shows the formation temperature of certain Ca-Al singulosilicates. These slags are gray. When high in SiO_2 and Al_2O_3, the texture is vitreous and the slags are viscous; if these constituents are low, the texture is more crystalline and the slags are more fluid. In the iron blast furnace CaO is very likely to be replaced to some extent by MgO from the flux or the gangue of the ore.

105. Iron silicates. These are formed in the making of wrought iron and in the reheating of muck bar, steel ingots, and puddling cinder. They are all more or less viscous and are seldom used in metallurgical processes.

106. Iron-calcium silicates. These are of the utmost importance in metallurgy, for they represent the slags made in the smelting of Cu, Pb, Ni, and other nonferrous ores. Fig. 30 gives the formation temperature of certain ferrocalcic silicates. MnO frequently replaces to some extent the FeO and MgO, and ZnO replaces the CaO. In general, in blast-furnace practice, singulosilicates are most common. Subsilicates are not often made, and sesquisilicates are made only in reverberatory practice, where

conditions are such that the slag can free itself more easily of entrained matte or metal. The presence of CaO, within limits, increases the fluidity of iron silicates.

107. Alumina. It is difficult to fix definitely the rôle of alumina in slags. When there is an excess of silica it acts as a base, and when there is an excess of base it acts as an acid. The condition under which one or the other takes place has not been definitely settled. Most metallurgists consider Al_2O_3 as an acid, and figure the charges for the furnaces on that basis.

108. Nonsilicate slags. These consist of a metallic oxide and an acid other than SiO_2, such as P_2O_5, Sb_2O_5, or As_2O_3, or of one or more oxides, such as PbO, CaO, FeO, etc. They are hardly ever formed in ordinary metallurgical practice. The purification of pig iron by the puddling process, the desulphurization of pig iron by MnO, certain special open-hearth processes, and the dry assay of gold, silver, and lead ores produce nonsilicate slags.

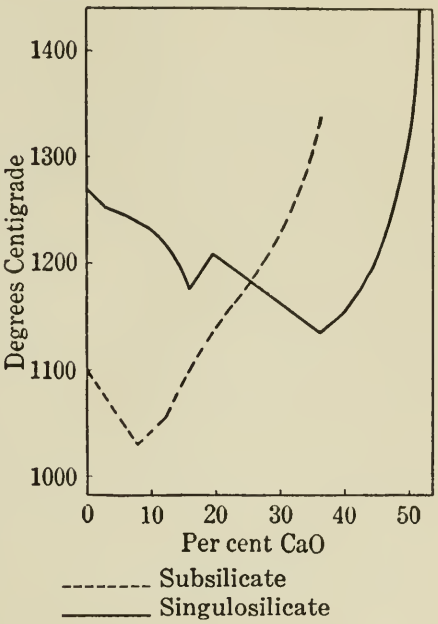

FIG. 30. Formation temperatures of Fe-Ca silicates

109. The use of waste slag. The disposal of slag, particularly in the crowded industrial centers, is a problem of no small moment to the metallurgist, and consequently many attempts have been made to utilize these waste slags. The most successful uses so far developed have been in the manufacture of slag cement, slag brick, and mineral wool. Slags from lead and copper blast furnaces have been cast in the form of bricks, blocks, and special shapes for use in metallurgical plants and in the construction of flues, chimneys, and certain parts of furnace foundations. Of course such brick cannot be used where any great mechanical strength or resistance to shock is necessary. Basic blast-furnace slag may be granulated, dried, ground, mixed with about 50 per cent of CaO, and molded into bricks. Some slags have been used as railroad ballast and as a road-building material. Mineral wool, made by blowing the molten slag into

fine threads, has been used in the place of other packing materials to protect fragile articles during transportation. A very large industry has been built up in the manufacture of cement from iron-blast-furnace slag. Slags produced in the refining of high-phosphorus pig iron in the basic open-hearth furnace have been used in the manufacture of fertilizers, since the slags often run as high as 15 per cent P_2O_5.

FLUXES

110. General. The chief fluxes employed in the smelting of nonferrous ores are iron oxides, calcium carbonate, silica, and fluorspar. As has been pointed out, these unite with the gangue, or worthless part of the ore, to form a fusible silicate or slag which does not mix with the matte or metal. The kind of flux which we must employ naturally depends upon the character of the ore. A high-silica silver-copper ore would probably require the addition of limestone and iron oxide to produce a slag of the required silicate degree, while a very basic lead ore would require the addition of silica. Barren fluxes, such as limestone and quartzite, should be avoided wherever possible, for it costs just as much to smelt barren material as it does to smelt valuable ore, and if we are to add a flux we might just as well add basic or acid material carrying some values in precious metals. For instance, if the ore requires silica, instead of adding crushed quartzite or ganister we should add some siliceous gold ore that could probably be obtained at a very low cost, — certainly for less than the cost of barren flux plus the precious-metal content. Certain ores or concentrates are termed "self-fluxing"; that is, they contain elements in the proper proportions to produce a slag of the required silicate degree without the addition of a flux. That such products are uncommon goes without saying.

111. Limestone. This is one of our most common fluxes in both ferrous and nonferrous metallurgy. Most of our copper and lead ores are acid — that is, contain excess silica — and must be fluxed with some basic material. Limestone is never used alone as a flux, but always with more or less iron oxide. Up to 30 per cent CaO it is used in slags, for limestone is cheaper than iron oxide and, for a given weight, neutralizes

more silica and therefore produces less slag. The dolomitic, or magnesian, limestones are objectionable, for the MgO gives rise to pasty, or viscous, slags. The matte or the metal made in connection with these does not settle as readily through them.

112. Iron oxide. Iron oxide is used alone or with limestone in the smelting of nearly all siliceous ores of copper, lead, and silver. Ordinary iron ore can be used, but when available it is usually high-priced. A far better form is *gossan*. When the ore near the surface of a sulphide deposit is attacked by ground waters loaded with oxygen and carbon dioxide, the copper, if present, is leached out and there is left behind a mixture of unaltered rock, iron oxides, gold, and silver. While of too low a grade to have value as an ore, this does have value as a flux, and the small amount of precious metal can be recovered.

The ferrosilicates are very fluid. Iron oxide slags containing as high as 65 per cent of FeO are fluid but have a high specific gravity, and in actual practice such a high percentage is seldom used. Matte and metal will not readily settle through them, and they corrode the acid lining of the furnaces. Iron oxide is never used alone, but always in combination with more or less CaO. In copper smelters, for example, the FeO ranges from 25 to 50 per cent, the CaO from 12 to 25 per cent, and the SiO_2 from 32 to 40 per cent. In lead smelters the FeO ranges from 24 to 52 per cent, the CaO from 0 to 30 per cent, and the SiO_2 from 28 to 36 per cent.

The addition of CaO to a ferrous silicate, while it lowers its specific gravity and lessens its dissolving power for metallic sulphides, increases its fusibility. The replacement of FeO by CaO is important. Iron singulosilicate ($2\,FeO \cdot SiO_2$) melts at 1270° C. As the FeO is gradually replaced by CaO the melting point is lowered, so that with 16 per cent of CaO and 53 per cent of FeO it is reduced to 1170° C. This may be offset, however, by the presence of other bases, such as MgO, Al_2O_3, ZnO, and BaO, for it is seldom that a slag consists solely of FeO, CaO, and SiO_2. On the other hand, the low melting point of such a slag is not always an advantage, for it may be viscous and flow very sluggishly. A furnace operating with such a slag would have a low capacity, and there would be an imperfect separation between the slag and the matte or metal.

113. Silica. Silica is used in the form of sandstone, quartzite, and quartz for fluxing basic or calcareous ores. Sometimes it is possible to use siliceous ores, but only when they contain free silica. Many siliceous ores contain silicates such as feldspar, hornblende, mica, etc. These silicates do not aid in the fluxing of the ores; in fact, they are a burden on the furnace, for heat must be supplied to melt them. The metallurgist should therefore handle his siliceous ores with caution.

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CHAPTER VI

PREPARATION OF ORES

114. General. The ore as it comes from the mine, whether it is from underground or from open-cut operations, varies in size from pieces several tons in weight down to the finest powder. The largest pieces must be broken in the *stope* or the quarry by block holing or by hand sledging until they are of a size to be conveniently handled by the loading apparatus. The smaller pieces are crushed mechanically to the proper size for metallurgical treatment. A blast furnace will not handle easily pieces of ore much larger than 6 inches in diameter, and roasters of the Wedge type are limited to material $\frac{1}{2}$ inch in diameter or smaller. For many of the hydrometallurgical processes the material must be pulverized until a large percentage of it will pass a 100-mesh screen (100 openings to the lineal inch). Fluxes such as limestone, iron ore, and silica are also mined in large pieces and must be considerably reduced in size before being mixed with the ore. This crushing or breaking, however, must be done intelligently, for the production of a large percentage of very fine material results in the formation of an excessive amount of flue dust in the roasting and reduction processes.

In the early days of metallurgy it was possible to treat the ore just as it was mined from the earth, or, better, with a small amount of preliminary breaking to bring it to furnace size. The demands of industry were not great, labor and fuel were cheap, and with the rich ores then obtainable the crude processes in use were successful. The metallurgist had at his disposal copper ores containing 10 per cent of Cu, lead ores containing 50 per cent of Pb, and silver ores containing from 50 to 100 ounces of Ag per ton. If we had to depend upon such sources for our metals today, industry would be in a sad state. Such rich deposits have now been exhausted, and industry is now dependent upon low-grade ores which have been enriched by one of the processes of ore-dressing, or concentration, until it can be profitably smelted.

In the early days, also, the metallurgist could not treat impure ores. Copper ores containing zinc, or zinc ores containing lead and iron, could not be profitably worked. Only as improvements were made in ore-dressing and in metallurgy could these refractory ores be smelted and the metals extracted at a profit.

115. Advantages of ore-dressing. An ore has been defined as a natural aggregation of minerals from which a metal or metallic compound can be recovered at a profit. When there is present a large percentage of worthless material, such as silica, limestone, or any of the rock-forming silicates, the ore cannot be economically treated by pyrometallurgical processes. The cost of handling such low-grade materials and the enormous quantities of fuel and flux necessary to slag and melt the constituents would be far more than the value of any metals which might be recovered. The process whereby the valuable minerals are concentrated in a smaller bulk and the worthless minerals rejected as waste, or tailings, is called *ore-dressing* or *concentration*. It may be that instead of separating the ore into a valuable product and a worthless one we are able to separate it into two or more valuable products and a tailing, as is the case with certain complex lead-zinc ores. Sometimes we seek to get rid of a constituent which, though not large in bulk, is of such a nature chemically as to seriously interfere with the subsequent smelting or leaching processes, — for example, zinc in a copper ore or iron in a zinc ore. The chief advantages of ore-dressing are as follows:

1. Most of the processes of ore-dressing are relatively cheap, and at a cost of from 60 cents to $1 per ton we can frequently transform an ore from a valueless product into one well worth the cost of smelting. For example, let us assume that we are smelting 100 tons of a lead-silver ore containing 9 per cent of Pb and 5 ounces of Ag per ton. In addition let us assume that the cost of mining is $2.50 per ton, that the cost of concentrating is 75 cents per ton, that the freight is $8 per ton, and that the 100 tons of ore will reduce to 10 tons of concentrate. We will also assume that it costs $17 per ton to smelt mine ore and $10 per ton to smelt concentrates. The losses in concentrating are taken as 10 per cent of the Pb and 15 per cent of the Ag. The losses in smelting mine ore are assumed to be 10 per cent of the Pb and 4 per cent of the Ag, and the losses in smelting

the concentrates are 5 per cent of the Pb and 3 per cent of the Ag. With these assumptions we can draw up the two following balance sheets:

Mining 100 tons of ore @ $2.50 per ton	$250
Freight on 100 tons @ $8 per ton	800
Smelting 100 tons @ $17 per ton	1700
Total	$2750
Return from 16,200 pounds of Pb @ 6 cents per pound	$972
Return from 480 ounces of Ag @ 60 cents per ounce	288
Total	$1260

That is, if such an ore were sent to the smelter it would mean a loss to the shipper of $14.90 per ton. On the other hand, the balance sheet of combined concentrating and smelting is as follows:

Mining 100 tons of ore @ $2.50 per ton	$250
Concentrating 100 tons @ 75 cents per ton	75
Freight on 10 tons @ $8 per ton	80
Smelting 10 tons @ $10 per ton	100
Total	$505
Return from 15,390 pounds of Pb @ 6 cents per pound	$923
Return from 412 ounces of Ag @ 60 cents per ounce	247
Total	$1170

That is, combined concentrating and smelting would bring a profit of over $6 per ton.

2. Even when the ore can be smelted directly it is often advantageous to concentrate it in order to save the cost of freight on the worthless constituents of the ore. Particularly is this true when the ore has to be sent long distances to the smelter.

3. In the treatment of complex ores we often effect a separation into two or more valuable products when the ore as it is mined could not be profitably smelted for either metal. For example, a sulphide ore containing 15 per cent of Pb, 10 per cent of Zn, and 4 per cent of Fe would be practically worthless; it would contain too much Zn for sale as a Pb ore and too much Pb and Fe for sale as a Zn ore; but by grinding, gravity concentration, and oil flotation we can often recover a large percentage of the metals as a lead concentrate containing 45 per cent of Pb and a zinc concentrate containing 50 per cent of Zn, rejecting as a tailing a large part of the worthless gangue and iron sulphide.

116. Principles of ore-dressing. Ore-dressing makes use of the physical properties of minerals and metals to effect a separation between the valuable and the worthless ones. The physical properties that may be taken advantage of in ore-dressing are as follows:

Specific gravity and settling power
Color and luster
Surface tension, capillarity, and flotation properties
Electroconductivity
Magnetic susceptibility
Hardness
Structure and fracture
Brittleness
Coefficient of friction
Greasiness
Change of mechanical properties with heat
Change of magnetic properties with heat
Decrepitation

Only the most important of these processes will be discussed here.

Differences in the specific gravity of minerals offer one of the surest and best ways of effecting a separation between them. The specific gravity of metals and minerals ranges from about 4 to 19, while that of the common rock-forming minerals, such as limestone, quartz, and the various silicates, ranges from 2.5 to 3.5. To accomplish a successful separation there should be a difference of at least 1.0 between the specific gravity of the valuable mineral and that of the worthless one.

The settling power of minerals in water, air, or some heavy solution is often taken advantage of. In water-concentration processes this is used in such machines as the Harz jig, the Wilfley table, the Richards classifier, and the Frue vanner.

Color and luster are of no use in the mechanical processes, but they are of the utmost aid in hand picking and sorting. Unless wages are very high a laborer can often earn his wage several times over by removing worthless or harmful minerals from the ore as it passes before him on a slow-moving conveyor belt. With certain classes of ores it is often advantageous to pick out rich material that can be shipped directly to the smelter without further treatment. The yellow of pyrite can readily be

distinguished from the resinous brown color of sphalerite, and the gray of slate from the milky white of gold-bearing quartz.

Oil flotation, one of the most recent of ore-concentration processes, and, for that matter, one of the most important, takes advantage of the property of selective oiling and surface tension. It has been found that under certain conditions sulphide minerals covered with an oil film will float on water, while silicate, oxide, and carbonate particles will sink.

Electroconductivity and magnetic susceptibility are used in such processes as the Huff, the Ball-Norton, and the Wetherill, and are of immense importance in the treatment of refractory ores. Iron, zinc, and titanium minerals are not very magnetic, but when exposed to high-power magnets they offer *differences* in attraction that may be taken advantage of.

The discussion of the preparation of ores will be taken up under the following captions: Crushing and Grinding; Screening and Classifying; Gravity Separation; Oil Flotation and Other Special Processes; Miscellaneous Processes.

CRUSHING AND GRINDING

117. General. We can divide the machines used in crushing and grinding into two classes: those used for breaking or coarse crushing and those used for pulverizing or fine grinding. The dividing line is usually taken at 1 inch in diameter. The breaking of an ore may be accomplished in two ways: (1) by the pressure of two surfaces that are being forced together, as in the Blake breaker or the gyratory crusher; (2) by the impact of two heavy bodies with the ore particle caught between, as in the ball or tube mill.

118. Breaking or coarse crushing. Gyratory crushers and Blake breakers are universally used for breaking run-of-mine ore for treatment in blast furnaces or reverberatories and for preparing run-of-mine ore for further reduction in ball, tube, and rod mills. Their field of work is from the largest pieces that can be gripped by the jaws down to pieces about 3 inches in diameter. Finer breaking than 3 inches can be more economically and efficiently done in other machines.

119. The Blake crusher, or breaker. Figs. 31 and 32 show in detail a Blake, or jaw, crusher. It consists of two jaws, one

fixed (1) and the other movable (2). The movable jaw is hinged at the top and is caused to approach and recede from the fixed jaw by means of a heavy toggle (3). This toggle is actuated by means of a vertical pitman rod (4) connected with an eccentric (5) on the main shaft of the machine. This shaft is driven by a belt and pulley (6) and has a heavy flywheel (7) to supply sufficient momentum to carry it over dead center and thus accumulate a reserve of energy sufficient to crush the largest piece that can be fed into the machine. The usual speed is 300 revolutions per minute. The two jaws are set at a slight angle, as indicated, so that the piece for crushing may be firmly gripped. Material fed at the mouth slowly

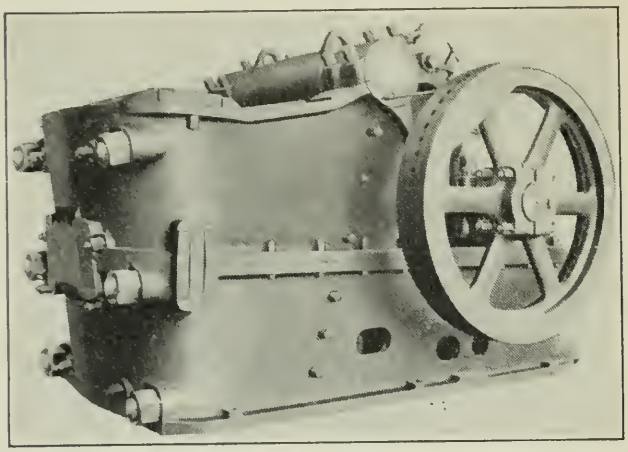

FIG. 31. Superior jaw crusher (60 × 48 inches)
Courtesy of the Allis-Chalmers Company

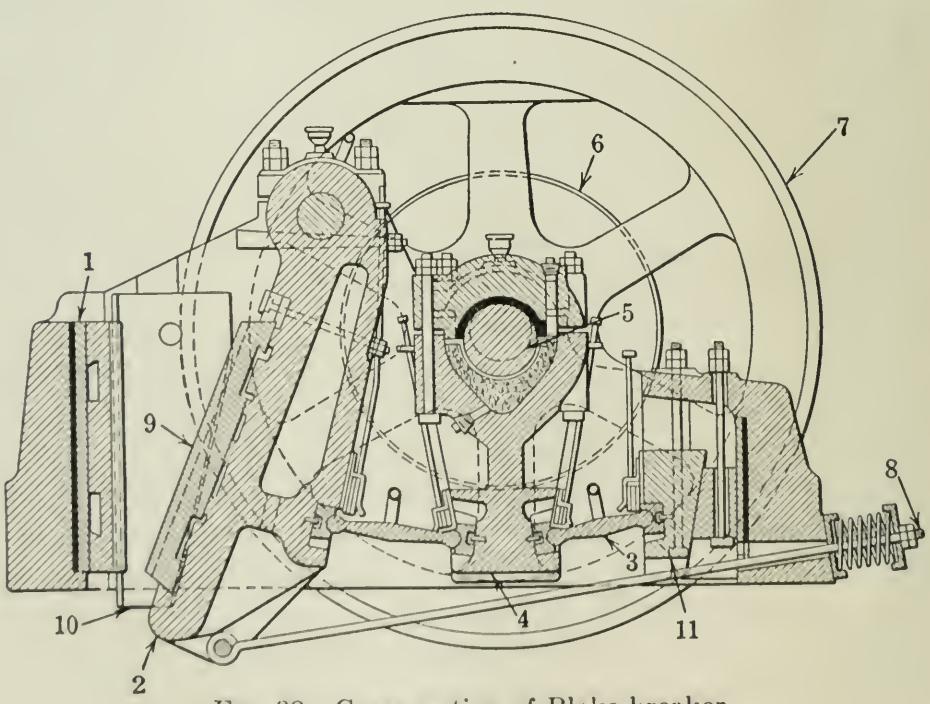

FIG. 32. Cross section of Blake breaker

descends, being crushed in the operation. As the jaw recedes, the particle drops, is caught as the toggles force the jaws together again, and is crushed still finer. A tension rod (8) at the bottom serves to hold the jaws firmly against the toggle in all positions and prevents the latter from dropping out when there is no pressure on the jaws. The receiving opening is called the *mouth* of the breaker, and the discharge opening is called the *throat*. Both the fixed jaw and the movable jaw, as well as the sides of the receiving opening, are lined with plates of manganese or chrome steel (9 and 10) to take up wear and to protect the frame of the machine from injury. As the jaws wear, the throat (and therefore the size to which the machine will crush) grows larger. This may be compensated for by lowering the bearing block (11) at the end of the toggles, thereby bringing them more nearly into line and forcing out the movable jaw. Table XIII gives data concerning this type of crusher.

TABLE XIII. CAPACITIES OF BLAKE, OR JAW, CRUSHERS

SIZE OF MOUTH IN INCHES	APPROXIMATE CAPACITY IN TONS PER HOUR IN CRUSHING TO THE FOLLOWING SIZES				HORSE POWER
	Inches	Tons	Inches	Tons	
7 × 10	1	2½	2	6	7
28 × 36	3	41	5	105	85
48 × 60	5	166	9	578	185
84 × 120	9	1100	14	2840	500

120. The gyratory crusher. This machine, as illustrated in Fig. 33, consists of a heavy frame or body surmounted by a spider (1), which carries the weight of the spindle (2) and the crushing head (3). The breaker head is lined with concaves (4) to protect the frame from wear. The crushing head is given a gyratory motion by means of the eccentric (5). This eccentric is driven through bevel gears (6 and 7) by means of the shaft (8) and the pulley (9). All bearing parts and gears are protected from dust and dirt and are supplied with oil under pressure. The gyratory motion causes the breaking head to approach and recede from the concaves, and owing to the fact that the spindle acts as a lever with the fulcrum at the top, it will cause a greater movement at the bottom than at the top. Any ore caught between the jaws (up to the limiting strength and

power of the machine) will be crushed. As large lumps are broken they fall to fresh bearing below and are finally ejected when they have been crushed small enough to fall through at the narrowest point. Raising or lowering the breaker head as

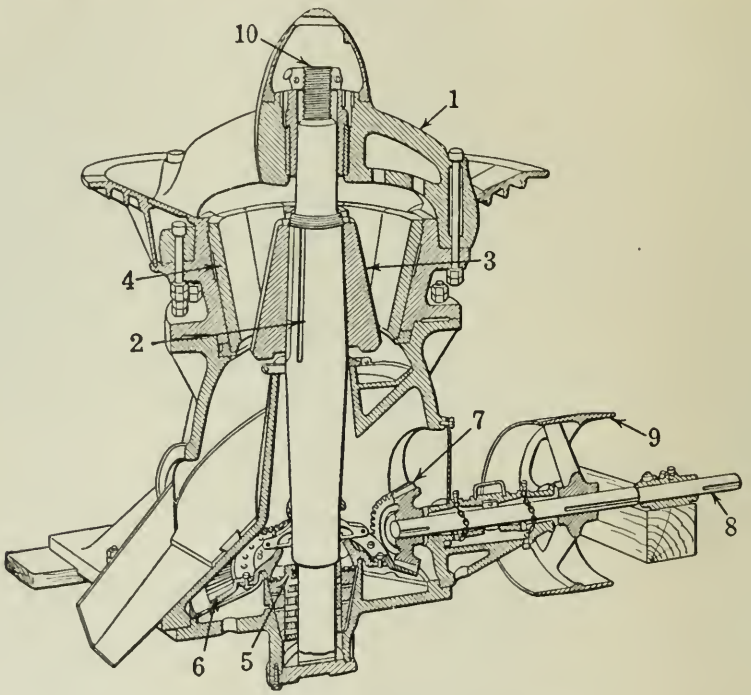

FIG. 33. Gates gyratory crusher

a means of adjusting the size of crushing is effected by means of the split nut (10). Experience has shown that the limit of the ratio of reduction is about 6:1. Table XIV gives data concerning this type of crusher. Fig. 34 shows a large modern machine with a capacity of 1500 tons per hour, built for a large copper company operating in South America.

TABLE XIV. SIZES, CAPACITIES, AND POWER OF GYRATORY BREAKERS

SIZE	SIZE OF RECEIVING OPENING (IN INCHES)	APPROXIMATE CAPACITY IN TONS PER HOUR IN CRUSHING TO THE FOLLOWING SIZES				HORSE POWER
		Inches	Tons	Inches	Tons	
3	7 × 22	$1\frac{1}{4}$	8	$2\frac{1}{2}$	18	20–30
$7\frac{1}{2}$	14 × 52	$2\frac{1}{2}$	55	5	120	75–100
10	24 × 82	4	155	6	244	125–150
18	36 × 114	6	500	8	750	150–200

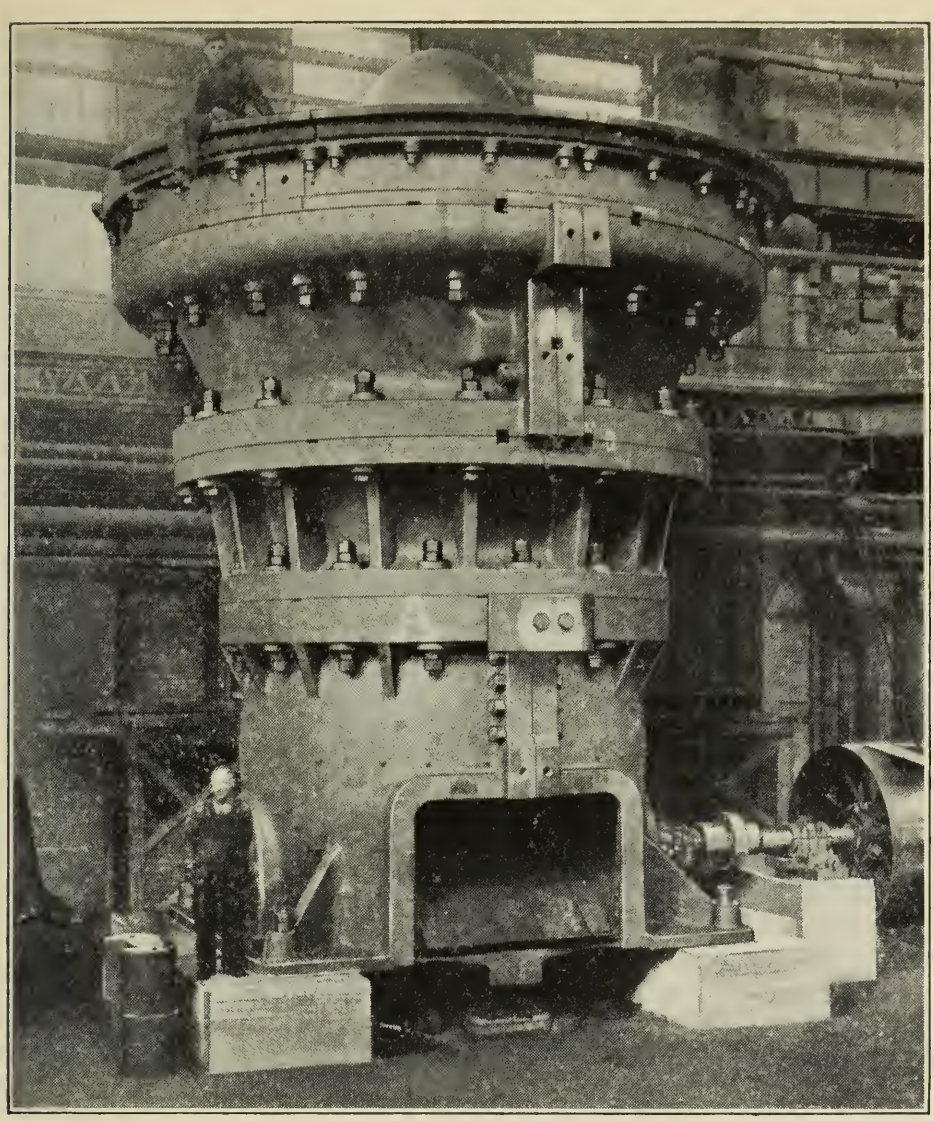

FIG. 34. Superior McCully gyratory crusher

121. The Symons disk crusher. In this machine the crushing is done between two disks. The horizontal type is shown in Fig. 35. It consists of two dish-shaped disks *a* and *b*, set with the concave sides facing each other. These disks are supported at a slight angle to each other and rotate in the same direction and at the same speed. The two disks are supported by two shafts, one of which is hollow and contains the other. The disks are held at an angle to each other by means of the ball-and-socket joint *g*. The outer disk is bolted to the bell-shaped end of the hollow shaft *c*, which runs in two fixed boxes driven by means of pulley *d*. The inner disk *b* is supported by the ball-and-socket

bearing *g*. This disk is not positively driven; it rotates only when ore is introduced between the disks. The crushing action is made more rapid by means of the eccentric *e*, driven by the pulley *f* in an opposite direction to pulley *d*. Crushing would be effected without this eccentric, owing to the angular relation of the shafts, but the use of the eccentric increases the capacity considerably. The crushed product is thrown outward, caught by the housing, and discharged at the bottom. The size of the product can be regulated by changing the distance between the crushing disks. At present the disk crusher is ordinarily used

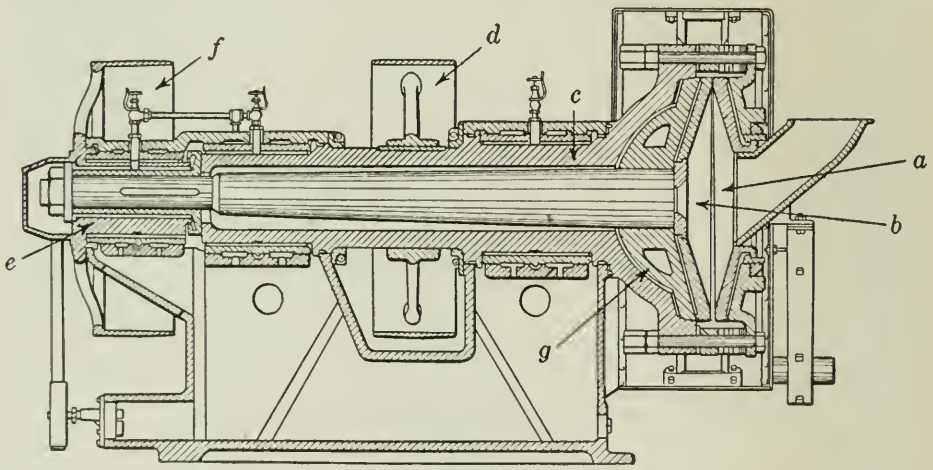

FIG. 35. Symons disk crusher

as an intermediate crusher, taking feed from gyratories or jaw breakers and crushing it to 1 inch or finer for grinding in ball or rod mills. A 48-inch Symons crushes from 1400 to 1750 tons of porphyry-copper ore per day, from 85 per cent on 1 inch to 80 per cent on $\frac{1}{2}$ inch, at a cost of about $0.00764 per ton.

122. The Symons cone crusher. This machine (see Fig. 36) has a greater ratio of reduction than any other coarse crusher on the market. It is the newest development in the field of coarse crushing and is an excellent machine for preparing coarse ore for fine grinding in ball or rod mills. It consists of a conical head gyrated (not rotated) by an eccentric which is driven through gears and a countershaft. The head is supported by a large socket bearing. This does away with any spiders or bearings above the crushing cavity. Opposing the thrust of the head is a crushing bowl threaded on its outer circumference for the purpose of raising or lowering. This bowl is held in place by means

of an adjustable ring threaded to fit the bowl thread and held down to the main frame by means of a series of heavy springs. Feed enters through the top and is distributed by a gyrating

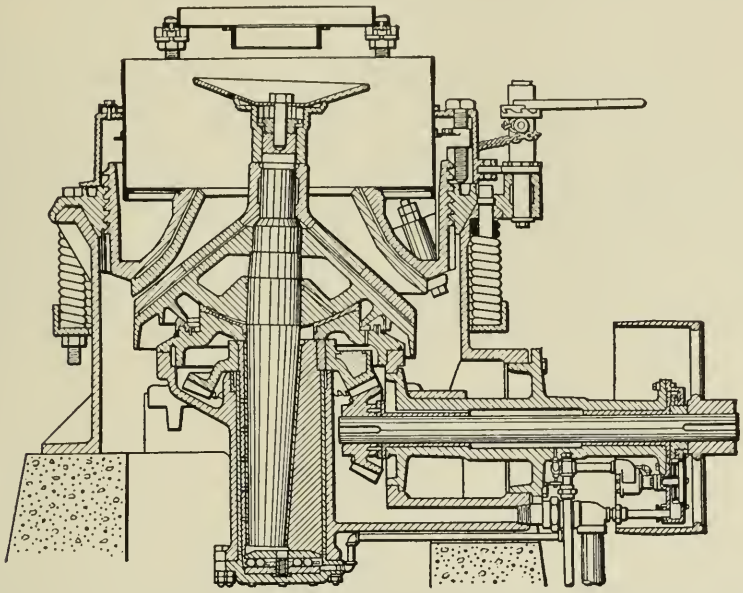

FIG. 36. Symons cone crusher

feed plate. The size of the product is adjusted by raising or lowering the bowl by means of ratchet-lever windlasses. Fig. 37 shows the new crushing action employed. The parallel zone regulates the size of the discharge absolutely, since the speed of gyration bears such a relation to the length of the parallel zone of the crushing head that no particle can escape before it has been crushed to this limiting size.

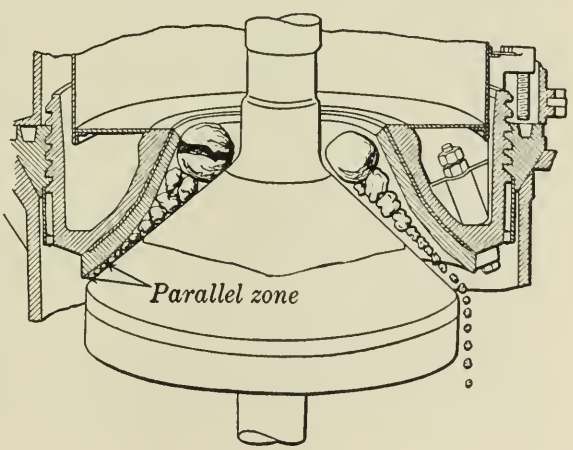

FIG. 37. Symons cone crushing action

123. Rolls. Although rolls are classified under coarse breakers, they work best as intermediate machines. Figs. 38 and 39 illustrate the common type. They consist of two iron or steel cylinders revolving in opposite directions. A lump of ore fed in at the top (provided it is

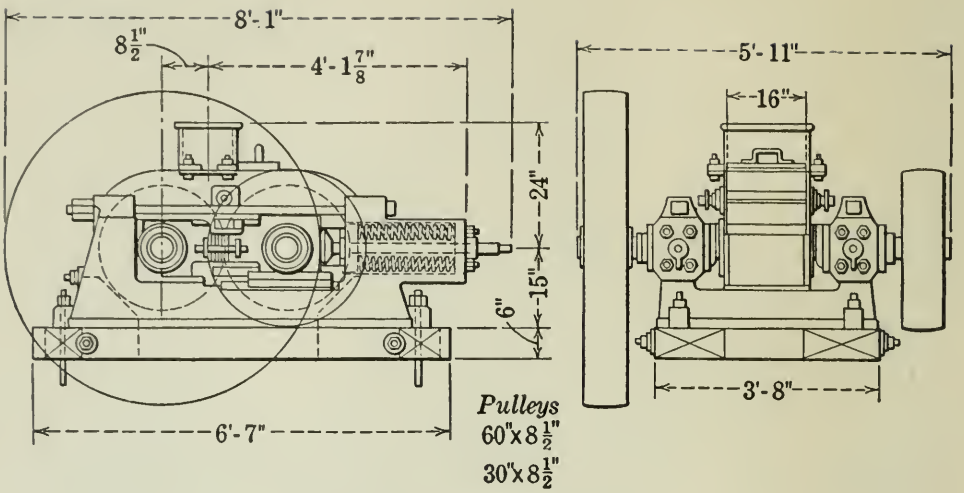

FIG. 38. Crushing rolls

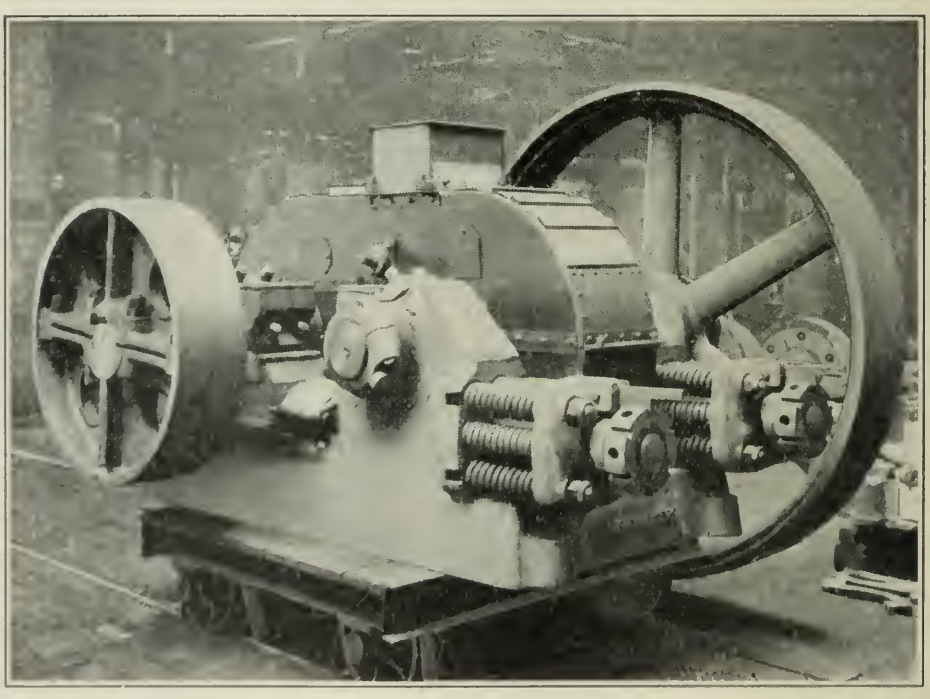

FIG. 39. Crushing rolls

not too large to be nipped) will be caught, drawn into the rolls, and crushed. One of the rolls is usually fixed, while the other is held in movable bearings by means of very heavy spiral springs. These furnish the requisite pressure for crushing and serve as a safety device in case tramp iron is caught between the rolls. Unless some such means were provided, the frame would be broken. The distance between the bearings of the two rolls, and hence the distance between the faces (the crushing size), can be regulated by means of shims. The rolls are covered with a removable shell of chrome or manganese steel to resist abrasion and wear. A housing incloses both rolls and prevents pieces of broken ore from flying out into the operating room.

Fine Grinding, or Pulverizing

124. The tube mill. In its simplest form the tube mill consists of a long steel cylinder supported on hollow steel trunnions. Such a mill is illustrated in Fig. 40. The shell is lined either with silex brick or with special ribbed steel plates. The grinding medium is flint or silex pebbles. The diameter of the mill varies from $3\frac{1}{2}$ to 5 feet, and the length from 12 to 22 feet.

The tube mill is fed by means of a spiral feeder mounted on the end of one of the trunnions. The scoop of this feeder lifts a quantity of pulp from the feed box at every revolution and, by means of a helix, forces it into the mill through the trunnion bearing. Pebbles may be fed in the same way without stopping the mill. The mills are driven at such a rate (from 22 to 30 revolutions per minute) that the pebbles are lifted part way up by the shell and then, under the influence of gravity, cascade over one another. The impact of these balls upon one another crushes or grinds any particles of ore which may be caught between them. Tube mills may be run either wet or dry, the former being the more common practice in ore-dressing.

The pulp as fed to the mill usually contains about 35 per cent of water. These mills are not efficient grinders on sizes larger than $\frac{1}{2}$ inch. As ordinarily used they receive feed from the coarse and intermediate crushers and grind it to 100 mesh or finer.

125. The Marcy mill. This mill differs from the tube mill in having a low pulp line. Instead of having the mill nearly half

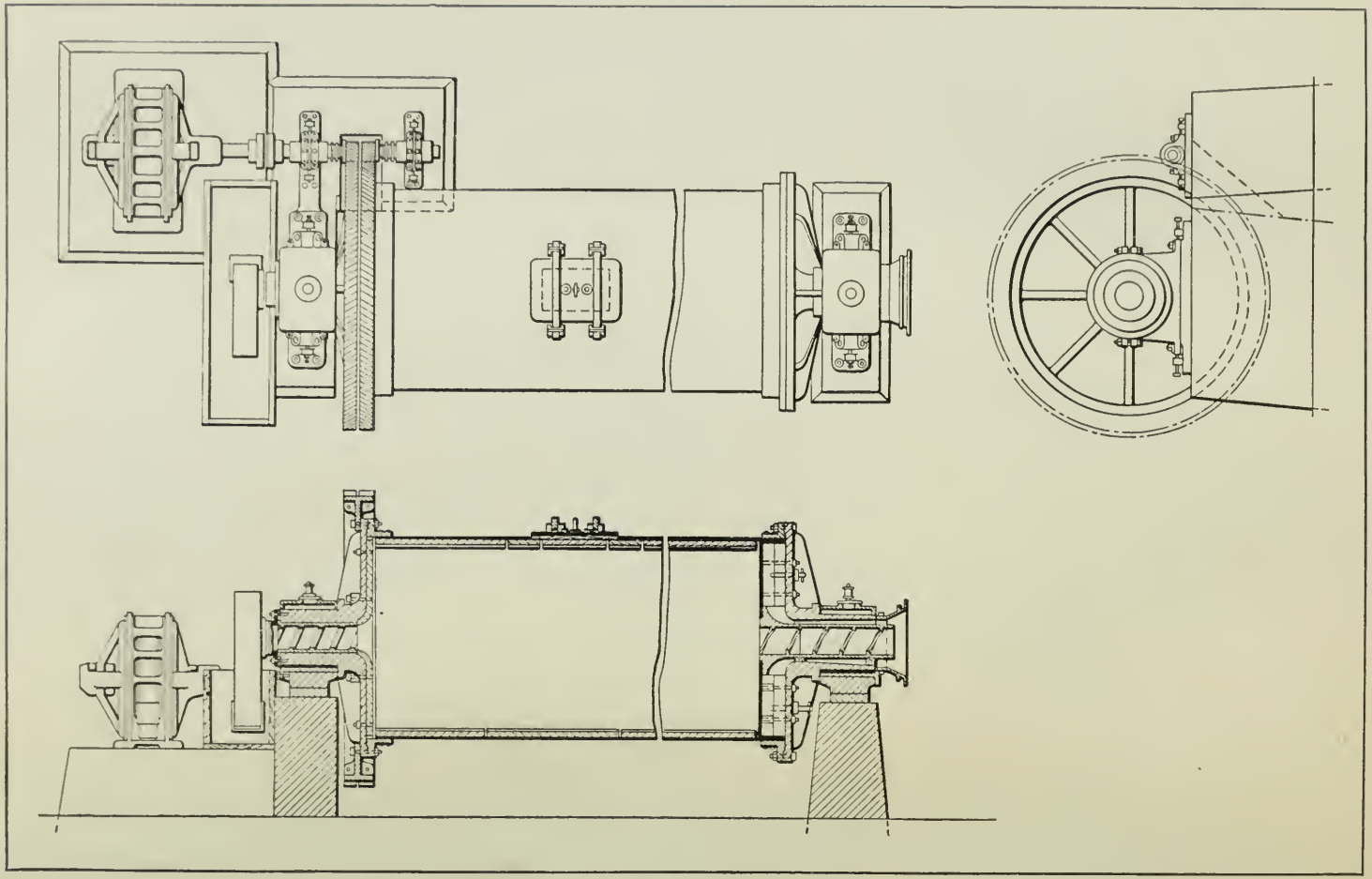

FIG. 40. Tube mill

full of ore and water, as in the overflow type, the Marcy mill operates with sometimes less than one foot of pulp in the bottom of the mill. The balls fall through the air in their cascade, instead of through a viscous pulp, and have a correspondingly greater crushing power. The mill is shorter and of more rugged construction, and employs steel balls instead of pebbles as the grinding medium. The Marcy mill is illustrated in Fig. 41. The steel shell *d* is lined on sides and ends with heavy liners of chrome or manganese steel *e*. It is supported, fed, and driven in much the same way as the tube mill. It is fitted with a diaphragm or discharge grate *c* with openings which vary from $\frac{1}{8}$ inch to $\frac{3}{8}$ inch, depending upon the fineness of grinding desired. This grate serves to keep the ore in the mill until it is crushed to the limiting size. Between the grate and the discharge end of the mill are radial lifters which elevate the material to the discharge trunnion and serve to keep the pulp line at its proper level. The balls are of chrome or manganese steel and vary from 2 to 6 inches in diameter. Ball consumption will vary from 2 to 6 pounds per ton of ore. Data on the Marcy mill is given in Table XV. The capacities are based on crushing medium-hard porphyry ore from $2\frac{1}{2}$ inches in diameter.

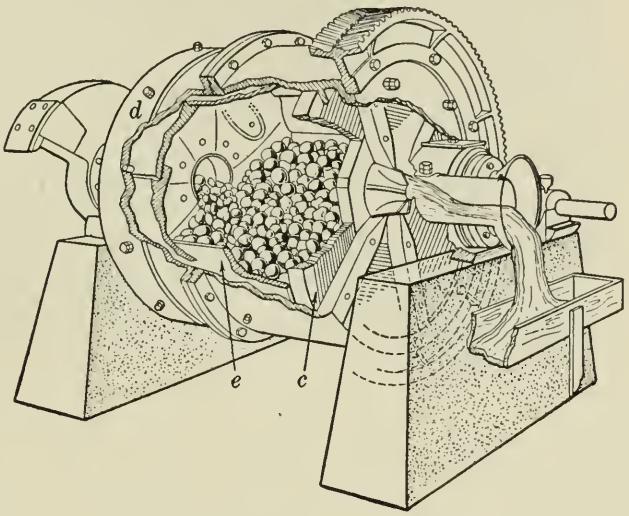

FIG. 41. The Marcy mill

TABLE XV. MARCY-MILL DATA

SIZE OF MILL		HORSE POWER	MAXIMUM BALL CHARGE, IN POUNDS	TONS CRUSHED IN TWENTY-FOUR HOURS TO 8 MESH	TONS CRUSHED IN TWENTY-FOUR HOURS TO 100 MESH
Diameter in Feet	Length in Feet				
3	2	6–8	1,200	20	4
5	4	30–40	6,800	125	25
7	5	100–150	17,650	655	130
8	6	150–225	28,500	1000	200

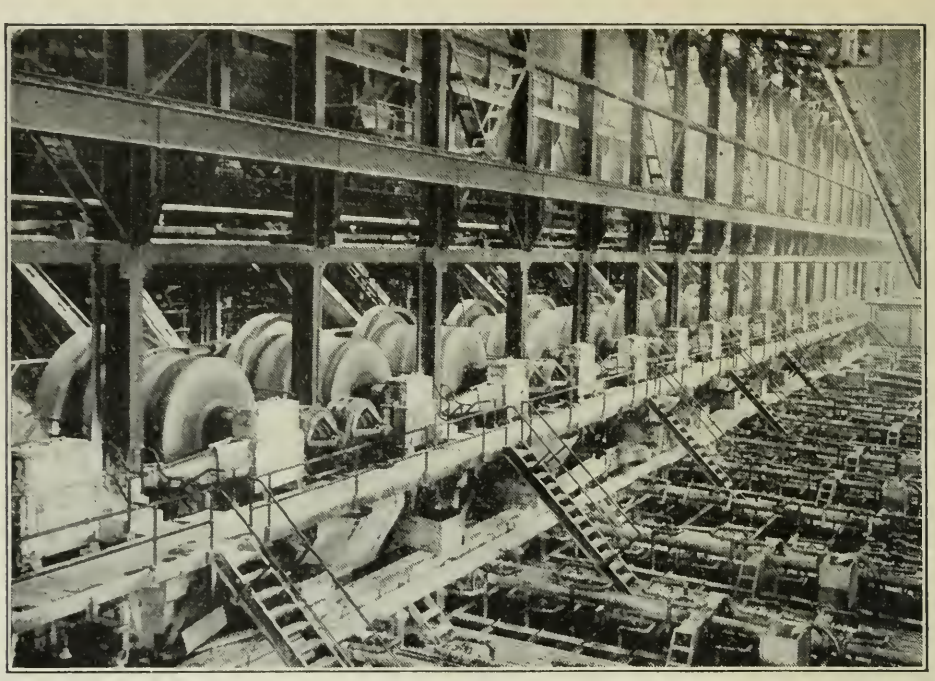

FIG. 42. Marcy-mill installation

126. The Hardinge conical mill. This mill is shown in Fig. 43. It consists of a conical steel shell lined either with steel plates or with silica brick, depending upon whether steel balls or silex pebbles are to be used as the grinding medium. The mechanical features of support, driving, and feeding are much the same as for the tube mill. The peculiar shape of the Hardinge mill permits an arrangement of balls for which the makers claim many advantages. As indicated in the sketch, the pebbles or balls are divided into zones by which the largest crushing bodies arrange themselves at the largest diameter and the smallest crushing bodies arrange themselves at the outlet of the mill. In this way the largest balls are able to work on the coarse ore as it comes into the mill, and the small balls finish the grinding operation. These mills are designated by the size of the cylindrical part. An "8 foot × 30 inch" means a mill having a cylindrical part 8 feet in diameter and 30 inches long.

127. The rod mill. This mill (illustrated in Fig. 44) is similar to the tube mill, but instead of balls or pebbles it uses rods of approximately the same length as the mill. The mill is lined with alloy steel liners of the clapboard or wave type. Rods from 3 to 4 inches in diameter are used, and it is found that when these are worn to about $\frac{1}{2}$ inch in diameter they break up into small

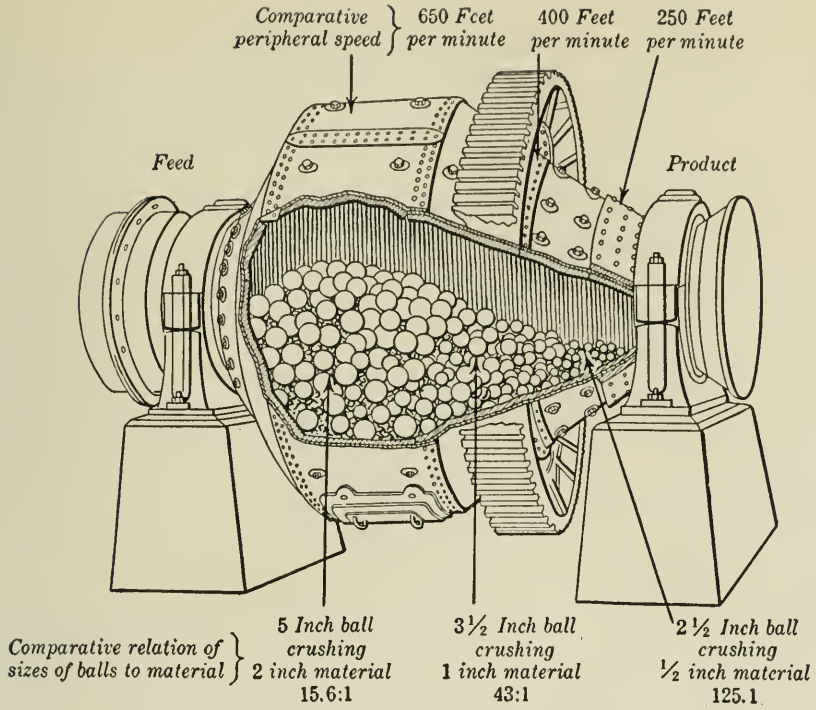
Comparative peripheral speed
650 Feet per minute
400 Feet per minute
250 Feet per minute
Feed
Product
Comparative relation of sizes of balls to material
5 Inch ball crushing 2 inch material 15.6:1
3½ Inch ball crushing 1 inch material 43:1
2½ Inch ball crushing ½ inch material 125.1

FIG. 43. The Hardinge conical mill

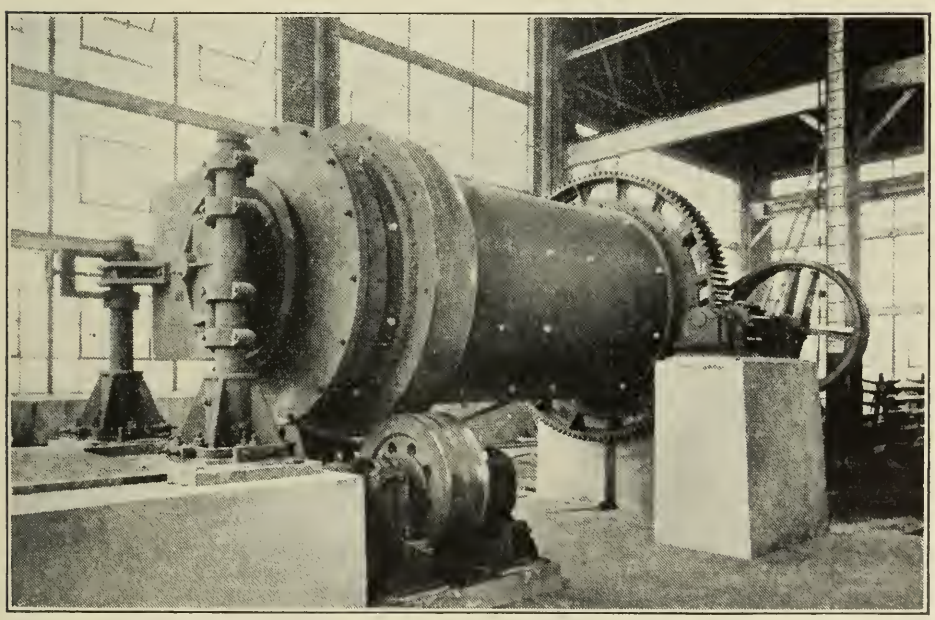

FIG. 44. The rod mill

Courtesy of Mine & Smelter Supply Co.

pieces and are ejected from the mill with the pulverized ore. A large capacity is claimed for this type of mill, owing to the fact that there is a greater surface of contact between the grinding medium and the ore. Two rods with a line contact have a much greater area than the sum of the point contacts between balls. The rod mill is a very recent type, and its field of work has not been definitely worked out. It is invading the field formerly occupied by the ball mill, and the indications are that it will do its best work in crushing 1-inch material to about 10 or 20 mesh. The consumption of metal in rods and liners is about the same as in the ball mill.

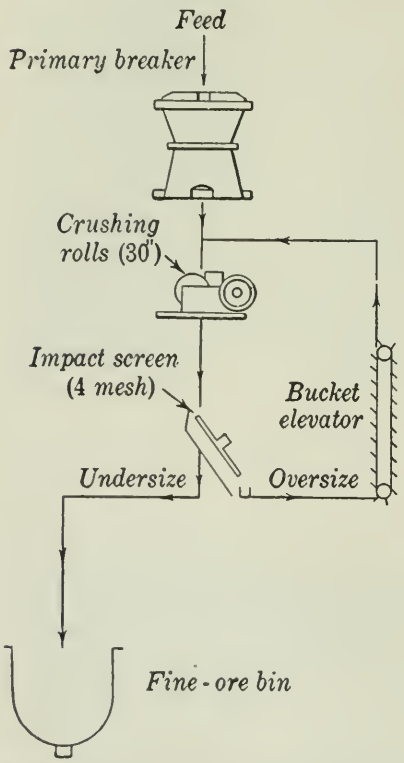

FIG. 45. Closed-circuit crushing

128. Closed-circuit grinding versus open-circuit grinding. In open-circuit grinding a mill receives feed, crushes it in one passage, and sends it on to the next crushing machine or to some concentrating process. If it is desired to crush to 10 mesh, and the machine is so set, the feed may or may not reach the desired degree of fineness. In closed-circuit work a classifier, or screen, keeps the material in the crushing circuit until it has been reduced to the desired fineness.

Fig. 45 shows a closed circuit often encountered in crushing practice. The 30-inch rolls are fed with material from some primary breaker and are set to crush this material to, let us say, 4 mesh. Owing to variations in operating conditions, such as hardness of the ore, moisture, etc., some of the material will pass through the rolls without being crushed to 4 mesh. The discharge of the rolls is received upon a 4-mesh impact screen. The undersize of this screen is a finished product and goes on to the fine-ore bin. The oversize of the screen is taken back, by means of a belt elevator, and fed into the rolls for a second time along with fresh material. This time it may be crushed to the desired fineness. The use of a combination of a ball or tube mill and a

Dorr classifier is very common practice for finer grinding. This method gives a high capacity, delivers a uniform product of any degree of fineness, produces less slime, and uses the power much more efficiently.

SCREENING AND CLASSIFYING

129. Grizzlies, or bar screens. The work of coarse separation is often carried out on grizzlies. Such a device is illustrated in Fig. 46. It consists of a series of heavy steel rails or bars placed at definite distances apart. The unsized material is fed in at the top, and under the force of gravity slides down over the bars, which are set at an angle of about 45 degrees with the horizontal. The fine ore, or undersize, falls through the screen and is gathered by an apron or a hopper for storage, or is fed upon a conveyor belt for transportation to some other part of the plant; the coarse material, or oversize, slides down the grizzly and falls over the edge into the next machine, or into a bin if crushing is complete. To make the ore slide as easily as possible the bars are always placed with their lengths in the direction of the steepest slope. Transverse bolts with separators keep the bars from sagging in case the span is considerable. The sides of the grizzly are walled in with heavy board or metal in order to confine the ore. The bars should be of such a cross section that the space between them will be wider at the bottom than at the top, to prevent wedging of the ore particles and *blinding* of the grizzly.

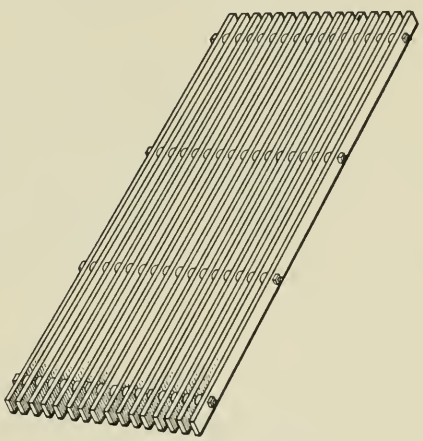

FIG. 46. A grizzly

130. Revolving screens, or trommels. The trommel is illustrated in Fig. 47. It may be built in the form of a cylinder, a prism, a cone, a pyramid, or a spiral; but since the cylinder is the most common form, it alone will be described. It consists of a central shaft of steel with two or more spiders with radial spokes. These spiders are fastened firmly to the shaft and terminate in T-shaped ends, which serve to support the screen sur-

face. The trommel is given a slight slope in the direction in which the ore is to travel. It revolves at the rate of from 8 to 30 revolutions per minute, depending upon the diameter of the cylinder and the fineness of separation desired. The ore is carried up one side of the trommel and falls back to the bottom of the screen, advancing slightly down the trommel. The fine material in its helical path through the trommel falls through the screen and is caught by an apron or a hopper and delivered onto a conveyor belt or into the next crushing unit. The oversize continues on through the trommel and is discharged from the lower end. Trommels may be run either wet or dry. Dry

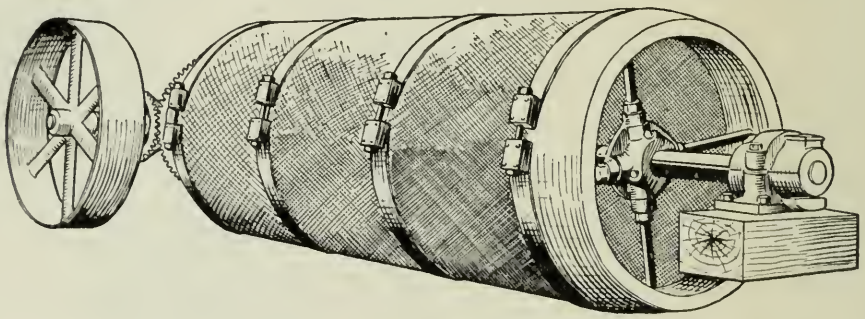

FIG. 47. A trommel

material causes an excessive dust loss, while damp ore screens badly. Therefore trommels are usually operated wet, with a spray pipe on the upcoming side.

The screening medium may be punched plate or woven-wire cloth. Plate is stronger, is less apt to break, and is more easily repaired than cloth. It cannot, of course, be used for the finer sizes. Wire cloth, on the other hand, has a larger percentage of opening and does not blind as easily. If there are acids or mineral salts present in the pulp to be screened, bronze or one of the alloys of copper must be used; in all other cases steel is the usual screening material.

131. The sieve scale. The successive screen sizes from the coarse down to the fine are called the sieve scale. Rittinger's scale, which starts with a 1-millimeter hole and works up and down from this point with 1.414 ($\sqrt{2}$) as the ratio, is the most common. A common sieve scale in use today, the Tyler, is given in Table XVI. In this country round holes are almost universally used in plates, and square holes in wire-cloth screen.

TABLE XVI. THE TYLER SIEVE SCALE

(Screen scale ratio, 1.414)

Openings		Mesh	Diameter of Wire in Inches
Millimeters	Inches		
26.67	1.050	—	0.149
18.85	0.742	—	0.135
13.33	0.525	—	0.105
9.423	0.371	—	0.092
6.680	0.263	3	0.070
4.699	0.185	4	0.065
3.327	0.131	6	0.036
2.362	0.093	8	0.032
1.651	0.065	10	0.035
1.168	0.046	14	0.025
0.833	0.0328	20	0.0172
0.589	0.0232	28	0.0125
0.417	0.0164	35	0.0122
0.295	0.0116	48	0.0092
0.208	0.0082	65	0.0072
0.147	0.0058	100	0.0042
0.104	0.0041	150	0.0026
0.074	0.0029	200	0.0021

132. The ring grizzly. Stationary-bar grizzlies for coarse screening usually work on run-of-mine ore. This contains all sorts of rubbish, such as pieces of wood and iron, sacks, fuse, etc., which tend to choke the openings between the bars. One of the most recent forms devised to overcome this difficulty is the Burch ring grizzly shown in Fig. 48. It consists of two disks, or heads, *a* mounted on a shaft *e* and connected by means of the rods *g*. Rings of two diameters are used. Spacers *d* are placed on the rods *g* to hold the small ring *c* in position. The large rings *b* are held midway between the small rings by means of lugs *i*. The grizzly revolves very slowly, the ore being fed on the top. The oversize falls down over the periphery of the rings

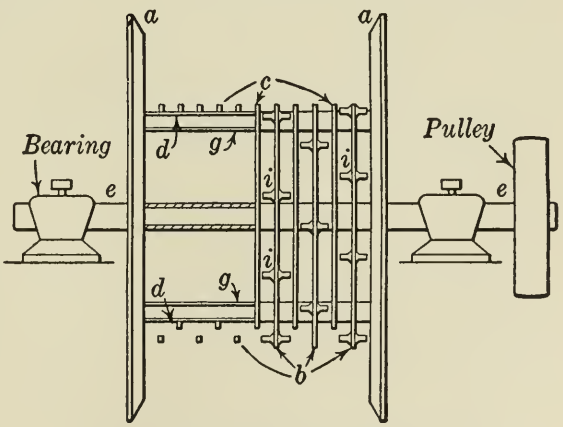

FIG. 48. The Burch ring grizzly

and may be caught by the apron; the undersize falls through into a hopper beneath the grizzly. There is more or less lateral movement to the rings, and this prevents blinding with damp ore or débris; and since there is considerably more space between the rings at the bottom than there is at the top, any material getting through at the top of the rings easily passes through the bottom.

133. The impact screen. This is the simplest type of flat inclined screen. It is illustrated in Fig. 49. The screening material is fastened to frame *s*, which is held in place by the spiral springs *e*. Ratchet *r*, as it revolves, imparts motion to the screening surface by alternately forcing the frame out against the springs and allowing it to fall back violently against four cushion stops. The ore is fed in at the top of the screen in much the same way as on a grizzly. This screen is not suitable for ore much coarser than 1 inch. It is usually operated dry.

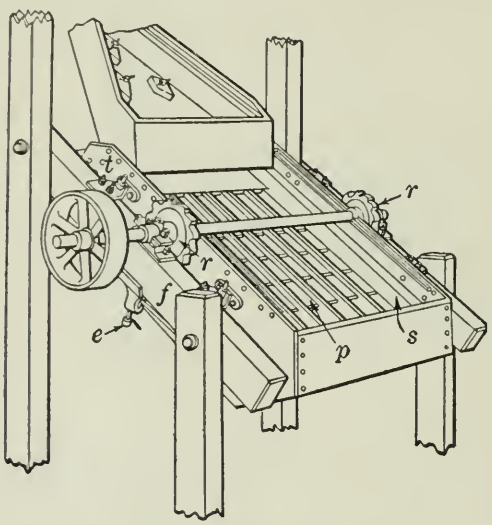

FIG. 49. The impact screen

Two new screens, the Hummer and the Mitchell, have recently appeared on the market. The screening surface is inclined as in the impact type. The Hummer actuates the screening surface by means of an electric vibrator, while the Mitchell does it by means of an eccentrically mounted shaft. They operate at a higher speed and with less amplitude of vibration than the impact type and are far more efficient devices. Repairs are somewhat less than in the impact type, there is less injury to the building structure, and the ore is on the screen during a greater part of its journey.

134. Classifying and settling. It is very difficult to screen fine material. Not only are fine-wire screens difficult and expensive to make, but their capacity and efficiency are low. It is impossible to screen effectively fine ore that is damp. For the finest grading, recourse must be had to a classifier or device which takes advantage of the ability of particles to settle

in water. The operation of these devices depends upon the following facts:

1. Of two particles having different specific gravities the one with the higher specific gravity will fall the faster.

2. A large particle will settle faster in water than a small particle.

3. Of the particles that will just pass a certain screen the flat particle will fall more slowly than the long, narrow grain, and this will fall more slowly than the round grain.

4. Of two liquids of different densities a particle settles more rapidly in the lighter.

If a number of particles of ore of various sizes, shapes, and densities are allowed to fall through water, the individual particles will form layers according to the laws stated above. There will be a bottom layer, containing coarse particles of the densest mineral and the largest particles of the less dense one, an upper layer, containing the smaller particles of the dense mineral and coarse particles of the less dense one, and layers (middlings) of varying composition in between.

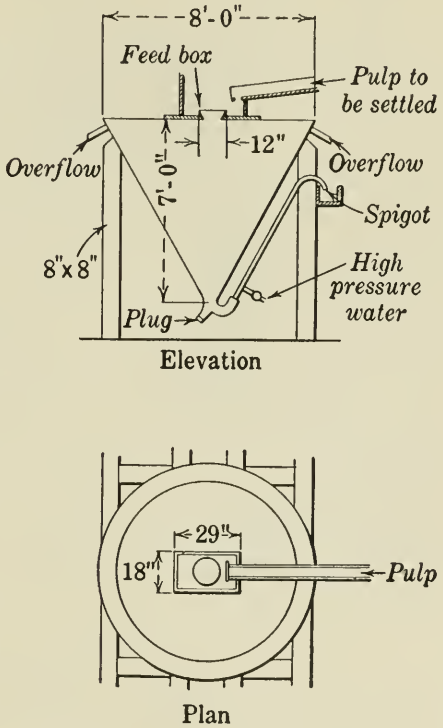

FIG. 50. The Callow cone

135. The Callow cone. One of the simplest of water-classifying devices is the Callow cone. It makes but two products — a spigot, or sand, and an overflow, or slime. Such a cone is illustrated in Fig. 50. It consists of a conical settling tank with a central feed compartment and an annular launder, or trough, around the lip of the cone to collect the overflow. At the apex of the cone is a spigot for the discharge of the settled sand. This may be in the form of a gooseneck to discharge the sand at a higher level than the apex of the cone and thus save mill-head. High-pressure water is introduced into the apex of the cone in sufficient quantity to induce a slight rising current

in the tank. Unclassified pulp is fed into the tank (which is filled with pulp to the level of the lip) through the central feed box. The coarse material settles to the bottom and is discharged, while the fine material overflows with the bulk of the water. Such a device is used mostly for separating a pulp into a sand and a slime or for partially dewatering such a pulp.

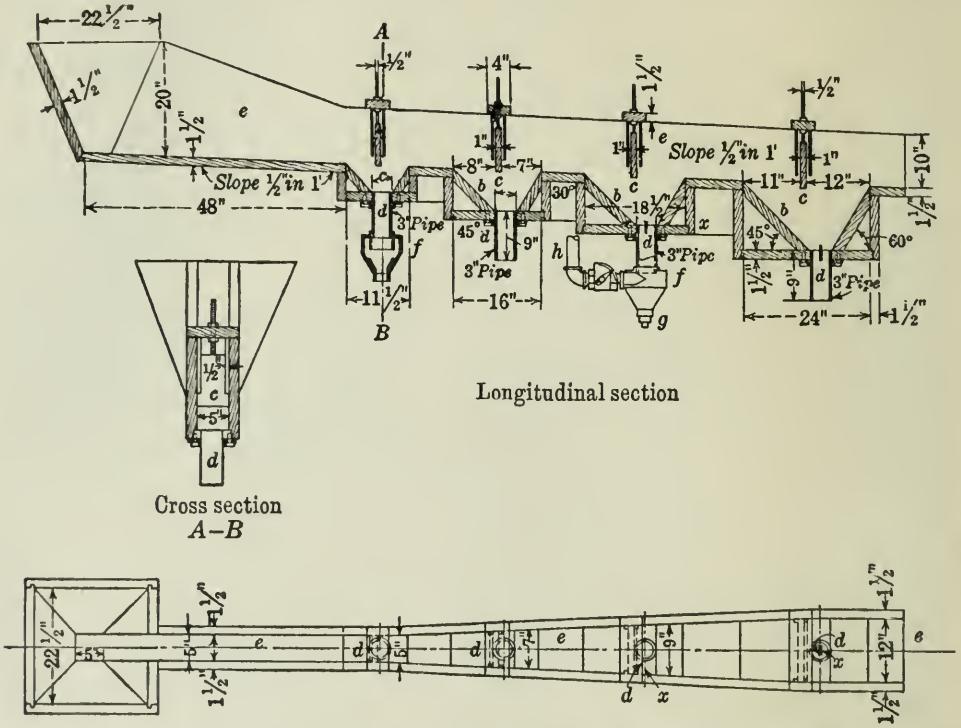

FIG. 51. The Richards deep-pocket hydraulic classifier

Courtesy of McGraw-Hill Book Company

136. The Richards deep-pocket hydraulic classifier. This classifier is one of the most efficient of the many classifiers on the market. It is particularly suited to close classifying in preparing for table treatment. It consists of a rectangular trough *e* with pockets *b* in the bottom and adjustable gates *c*. The sorting columns consist of vertical iron pipes *d* with vortex fitting *f*, which gives a whirling motion to the water admitted at *h*. The pulp enters the feed box at the left. Grains that are heavy or large enough to settle against the rising current in the first pocket do so and are discharged through the spigot, which is free-running. The rest of the material flows on to be classified into other sizes depending upon the relative rising currents in the next boxes. The finest slime overflows at the end of the trough.

137. The Dorr classifier. This classifier is used chiefly for dewatering pulps or for separating them into a slime product and a sand product. Fig. 52 illustrates the duplex type. It consists of a rectangular tank with a sloping bottom. In this tank two frames of scrapers, or rakes, actuated by a bell-crank mechanism mounted above the tank, move the settled material up the slope. While one scraper is moving up the slope the other is returning to the initial position, thus balancing the thrusts.

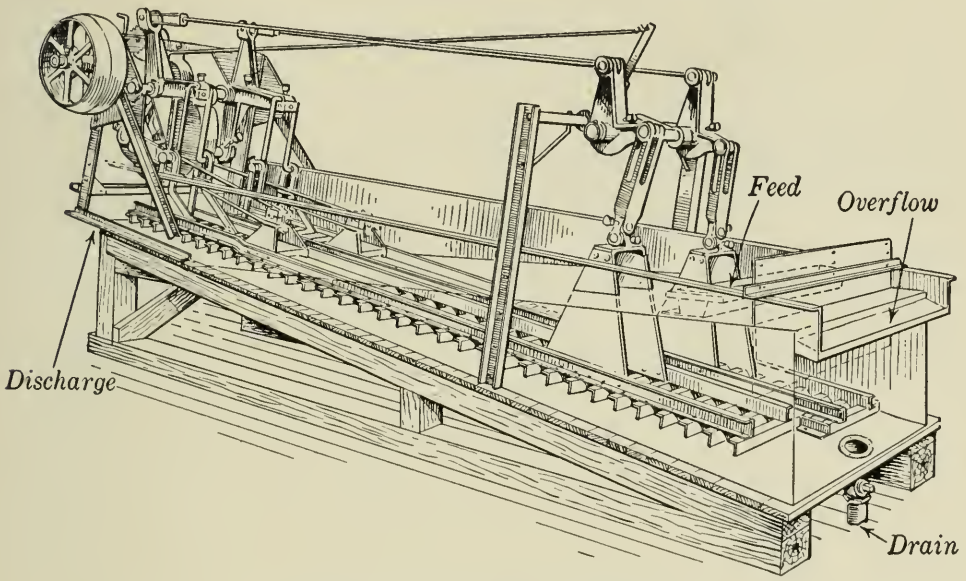

FIG. 52. The Dorr classifier

Unclassified pulp enters by means of a feed launder, about a foot from the overflow lip. The coarse material settles immediately to the bottom of the tank, is slowly moved up the incline and cleaned thoroughly of slime in its passage, and is finally discharged at the top. The position of the water level, as indicated, leaves a space of three or four feet in which the sand can be drained of water. The water and the fine slime which does not settle are discharged at "overflow." The rakes operate at from twelve to thirty strokes per minute. Any degree of fineness in the overflow may be obtained by suitable adjustments of the speed of the rakes, the slope of the bottom, and the density of the pulp in the tank.

138. The Dorr thickener. Fig. 53 illustrates the usual type of Dorr thickener. It consists of a cylindrical tank from 10 to 60 feet in diameter and from 8 to 15 feet in height. In the

center is suspended a vertical shaft supporting four radial arms. This shaft is revolved at a slow speed (approximately 10 feet per minute at the outer end of the long arm) by means of a worm gear. To the radial arms are attached rakes or plows so inclined that they slowly work the settled material toward the center of the tank. Around the shaft is a small cylindrical feed box dipping below the surface of the water in the tank. Around the tank is an annular launder to take away the clear water that overflows from the lip of the tank. The arms are set at a slight angle to the horizontal in order to build up a hopper-shaped bottom in the tank and to facilitate the discharge of the settled material. In the center of the bottom of the tank is a valve, or spigot, for the discharge of the settled material. The power required to operate such a tank varies from $\frac{1}{4}$ to 2 horse power. These machines are efficient settlers and are widely used in cyanide plants for thickening pulps, in ore-dressing plants for dewatering concentrates or preparing pulps for filtration, and in general practice for the removal of water. The tractor type, in which the outer ends of the arms are supported by trucks, has been built as large as 300 feet in diameter.

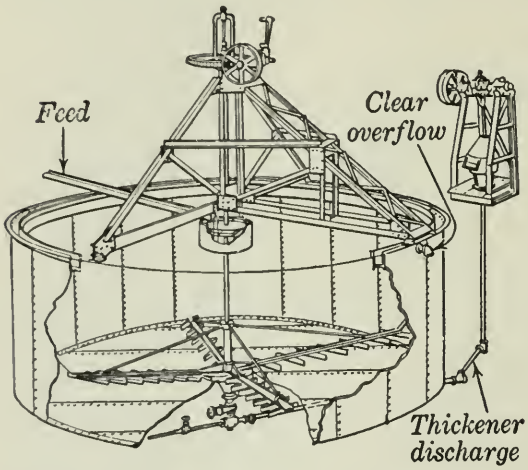

FIG. 53. The Dorr continuous thickener

GRAVITY SEPARATION

139. General. Most of the machines for separating the raw ore into a valuable concentrate and a worthless tailing take advantage of the difference in specific gravity of the different minerals. The principles involved have already been outlined under "Screening and Classifying." The preparation of the raw ore, after crushing, grinding, and sizing, is usually conducted in three stages, or cycles: coarse-sand treatment, fine-sand treatment, and slime treatment. It is obvious that if the mate-

rial being treated contains coarse pieces of free mineral 1 inch in diameter, it is better to try to recover some of this in the early stages of crushing than to pulverize it to 100 mesh and then try to recover it. None of our concentration processes are perfect, and some of this mineral would inevitably be lost. On the other hand, some of our ores, such as the disseminated copper ores of the Southwest or some low-grade gold ores, do not contain any coarse mineral or metal; and the first two stages of concentration are best omitted. Such material is crushed and ground to a fine slime before any leaching or concentration is attempted.

140. Concentrates, middlings, and tailings. If an ore consists of only two minerals, — one valuable and the other worthless, — with relatively large pieces of the former embedded in the latter, concentration is fairly easy. The ore can be crushed fine enough to free the coarse mineral and can then be separated by water concentration into a concentrate, or valuable portion, and a tailing, or worthless portion. Usually the problem is not so simple. There may be two or more valuable minerals, or the first crushing may not free all of the mineral. For example, a piece of quartz 1 millimeter in diameter may contain very small grains of galena, sphalerite, or pyrite. Concentration of such an ore will yield concentrates of the various minerals, a product of intermediate specific gravity called a middling, and a tailing. The tailing may be rejected as worthless, but the middling must be re-crushed and re-treated on a machine adapted or adjusted to finer concentration.

141. Principles of jigging. If a mass of minerals of different specific gravities but of about the same size, supported on a screen of a finer mesh than the smallest particle, is dipped suddenly into a tank of water, a stratification of the minerals will result. Owing to the resistance of the water, none of the minerals can follow the screen as fast as it descends. The densest minerals will fall the fastest; so that after a series of such pulsations three layers will form upon the screen: first, a layer of these heavy minerals; next above, a layer of less dense minerals; and on top, a layer of light minerals, gangue or tailings. For the concentration of ore ranging in size from 20 to 2 millimeters the jig is the only machine that covers the entire field well. For the concentration of ores coarser than

about $\frac{1}{2}$ inch in diameter, there is no machine that can compete with it. The separation can be effected by moving either the bed of ore or a column of water so that jigs may be divided into fixed-screen jigs and moving-screen jigs.

142. The Harz jig. Fig. 54 illustrates the Harz jig. It consists of a hopper-bottomed tank *a* divided by a longitudinal

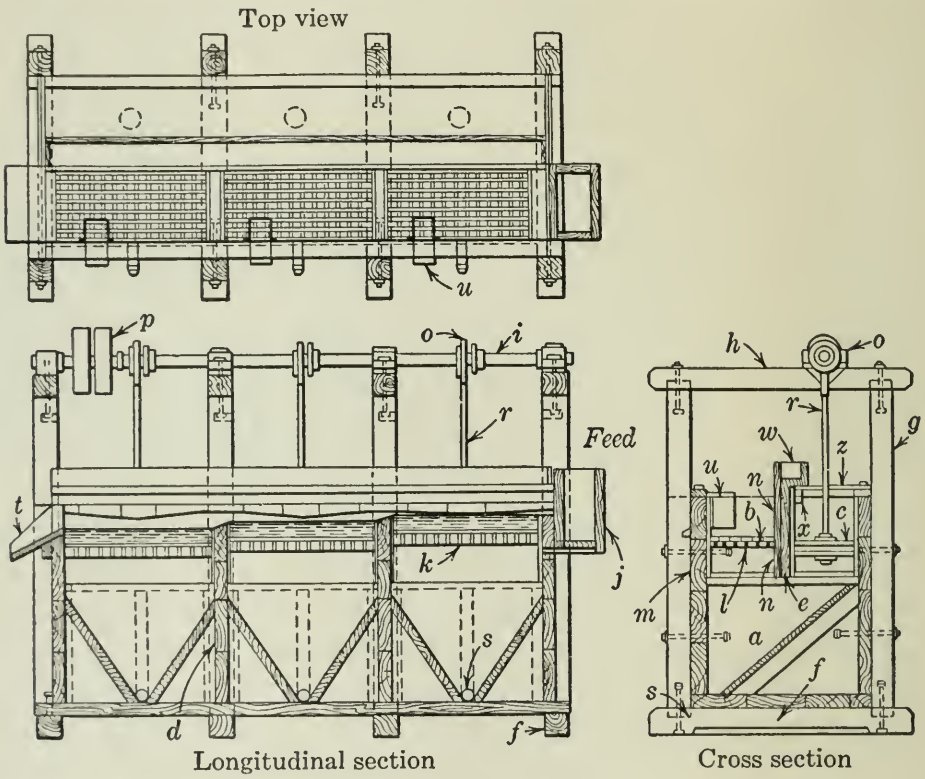

FIG. 54. The Harz jig

Courtesy of McGraw-Hill Book Company

partition *e* into a plunger compartment and a screen compartment. This partition extends only part way to the bottom of the tank, so that there is free communication between the two compartments. The screen *b* (which is fixed) serves to support the mass of mineral under treatment. The plunger *c* fits loosely into its compartment and is given a reciprocating motion by means of a pitman *r* and eccentric *o*. On the down, or pulsion, stroke the water is driven through the communicating space between the two compartments and up through the screen, lifting the bed of ore. On the return, or suction, stroke the mineral falls back to rest on the screen. This brings about

the condition outlined in the previous paragraph and causes a stratification, or layering, of the mass. Some of the denser minerals in the lower layer, broken by attrition into particles finer than the limiting size of the screen, fall through this into the bottom, or hutch, of the jig and may be withdrawn either continuously or intermittently by means of a spigot *s*. The jig may be divided longitudinally into two or more compartments, each with a separate plunger and screen chamber. With a slight drop between the successive compartments the jig becomes a continuous machine. A mixture of sized ore and water enters at *j* and is treated in the first compartment, where a

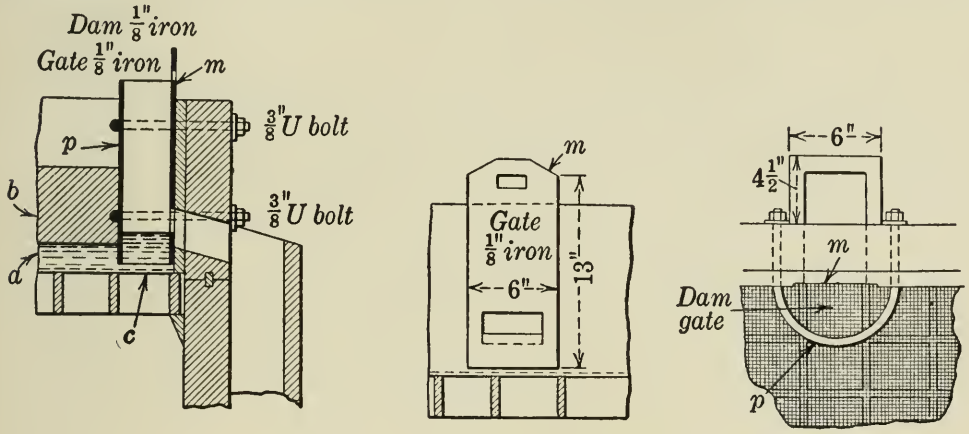

FIG. 55. An automatic discharge

concentrate is made and withdrawn by means of the automatic discharge on the side. Ore which does not find its way into the lower layer overflows with the gangue into the second compartment, where the treatment is repeated and another and lower-grade concentrate is made. After several such treatments the material overflows the end of the jig at *t* and is discharged as tailings or reground for treatment on other machines.

The concentrate and middlings are withdrawn by means of a continuous discharge located on the side of each compartment. Such a discharge, and the type commonly used in jigs, is illustrated in Fig. 55. It consists of a rectangular opening cut in the outside wall of the jig compartment just above the screen. It has an adjustable slide *m*, which has a rectangular opening 4 inches by $1\frac{1}{2}$ inches. A semicircular dam *p* extends from just above the level of the pulp in the jig to a short distance above the screen. This distance will be determined by the size of the

feed being treated. It should be such that a stream of material four or five grains deep can pass under the dam and make an easy discharge. If it should clog, valuable material is likely to find its way into the tailings. In the operation of the jig, concentrate *a* and tailings *b* will separate out and dam *m* will be so adjusted that the weights of columns *a* and *b* will be greater than the weight of column *c*, causing a flow of concentrate into the discharge compartment. It will overflow continuously into a concentrate launder. By adjusting the height of discharge, rate of pulsion, amount of water, and fineness of feed, corresponding changes can be brought about in the tenor of the concentrates, middlings, and tailings produced.

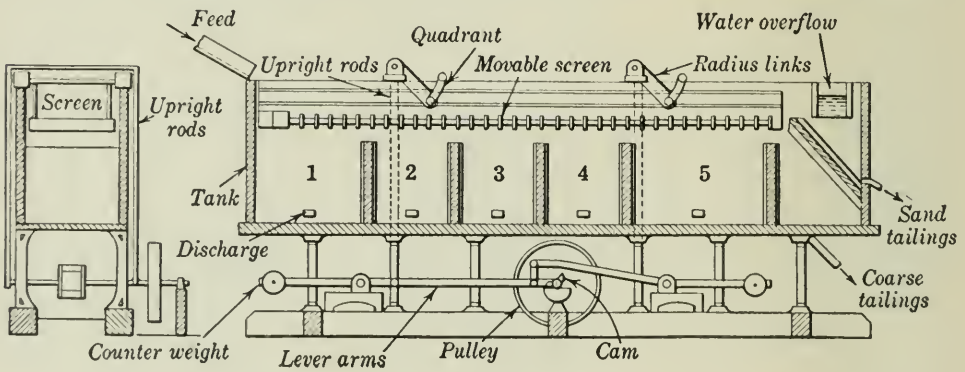

FIG. 56. The Hancock jig

On an average the capacity of a Harz jig may be taken as ranging from 0.5 to 2 tons per square foot of screen area per twenty-four hours.

143. The Hancock jig. This is a jig of the moving-screen type and is best adapted to the concentration of comparatively coarse ore. The Hancock jig is illustrated in Figs. 56 and 57. It consists of a jig box, or tank, divided into six compartments, five of which will form hutch concentrate and the sixth a tailing. The tray, or movable screen, holds the mass of ore during treatment and is suspended in the tank by means of the upright rods. A driving mechanism under the tank gives this tray a combined vertical and horizontal movement. This motion causes the ore to pass over the screens from the feed end to the discharge end, and the vertical component of this movement serves to bring about a stratification of the minerals in the tray. The size of the screen opening increases progressively

toward the tailing end of the jig. The heaviest minerals go to the bottom layer and pass through the screen into one of the first three hutches, the middlings drop into the fourth or fifth, while the tailings overflow at the end of the tray as indicated.

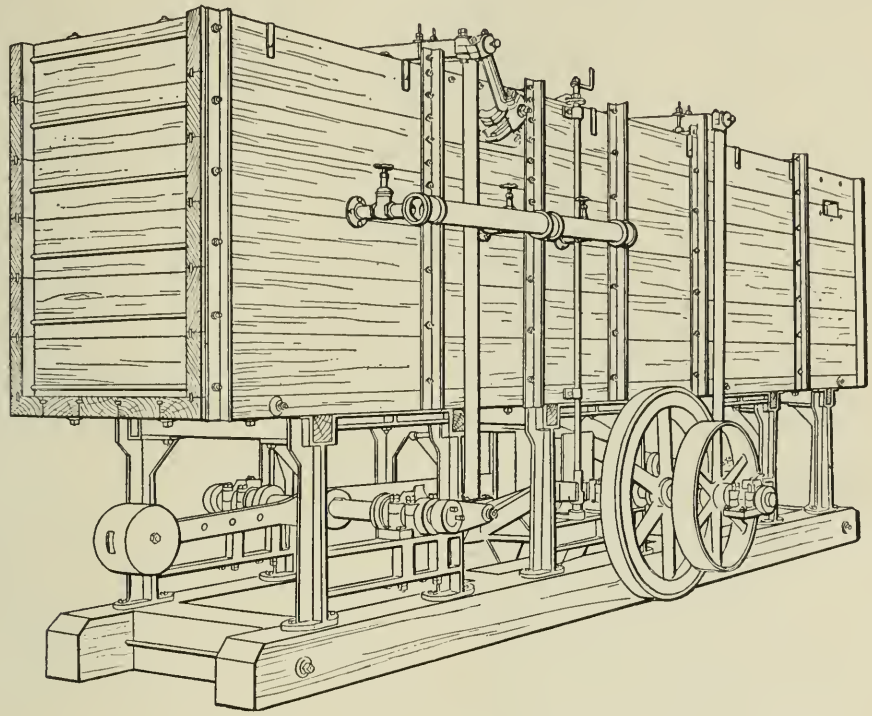

FIG. 57. The Hancock jig

144. Theory of table concentration. Let us assume that we have a smooth inclined surface h making an angle α with the horizontal as illustrated in Fig. 58. Let us place on this surface two cubes a and b of different densities and different sizes. Angle α is so small that the pull of gravity alone will not move these cubes down the plane. A sheet of water flowing down over this plane, deep enough to cover the cubes, will exert more force on the less dense and larger cube b than on cube a. The frictional resistance of both cubes will be approximately the same. By adjusting the rate of flow of the water and the inclination of the table, a point may be reached at which the

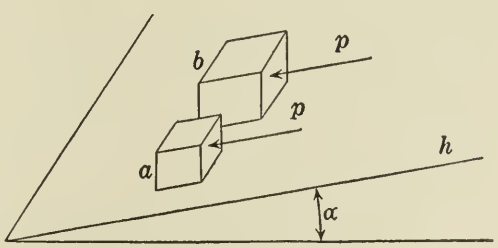

FIG. 58. Table concentration

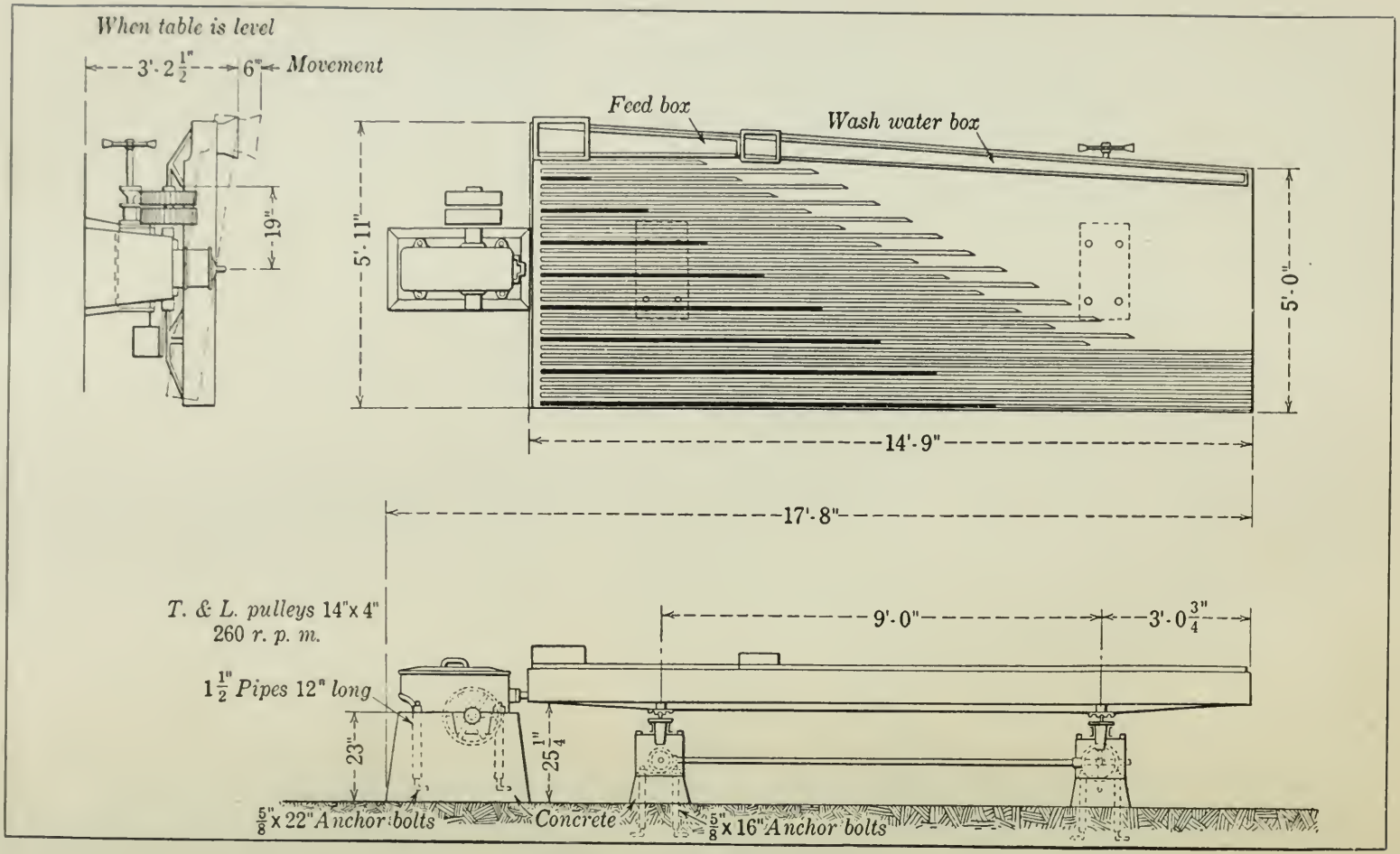

FIG. 59. The Wilfley table

larger cube will move down the plane but the smaller cube will remain unaffected. This constitutes the basic principle of *table* and *vanner* concentration.

145. The Wilfley table. The Wilfley table is illustrated in Fig. 59 on page 112. It is an endwise-reciprocating table with a roughly rectangular deck, or surface. It is inclined slightly at right angles to the line of reciprocation, so that a thin film of water and finely crushed ore may be made to flow across it. The head motion causes the deck to reciprocate at the rate of from 250 to 375 strokes per minute, each with an amplitude of from $\frac{1}{2}$ inch to $1\frac{1}{2}$ inches, depending upon the size of the material to be treated. The table rests upon a heavy foundation, and by means of an adjusting wheel located at the back it can be given any degree of inclination. The deck is firmly braced and covered with heavy linoleum on which are laid riffles, or narrow strips of wood, as indicated in the sketch. The longest and deepest riffle is placed along the lower, or tailing, side and extends the whole length of the table. These riffles taper off and end on a diagonal line as indicated. The pulp (about 5 parts of water to 1 part of ore) enters the table at the feed box. Wash water is added as required along the feed-box side of the table. Under the combined action of the water current and the impulses of the head motion the material will divide itself into several zones, as indicated in Fig. 60. The finer, heavier minerals will work along the bottom of the riffles, across the "plateau" of the table, and be discharged at the concentrate end. Mineral of decreasing specific gravity and increasing size will be discharged in the first few feet of the tailings side. This will constitute a middling and will be sent on for re-treatment. Finally, along the remainder of the tailings side, the finest slime carried by the water, together with large pieces of gangue, will be discharged. The capacity of a standard table varies from 15 to 50 tons per twenty-four hours, depending upon the size of the feed and the recovery of mineral which must be made. This

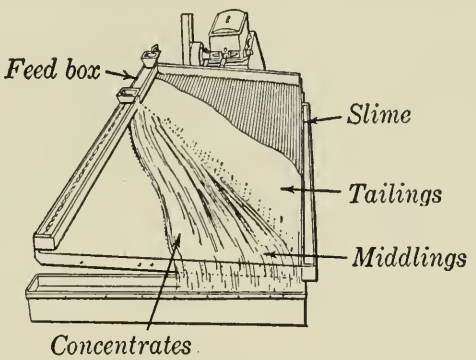

FIG. 60. The action of the Wilfley table

table is not adapted to the concentration of coarse material. Its field of work is the treatment of ores ranging from $\frac{1}{4}$ inch in diameter to about 100 mesh. Coarser material is best treated on jigs and finer material on vanners or by the oil-flotation process.

146. The Frue vanner. The finest material cannot be handled on machines of the Wilfley-table type, because the agitation is too violent. Much of the fine, free mineral is kept in suspension and carried away with the tailings. For the treatment of the finest slimes, ranging from 60 mesh down, the vanner has been and still is used. Wherever sulphide material is involved the work can now be done much better by means of oil flotation,

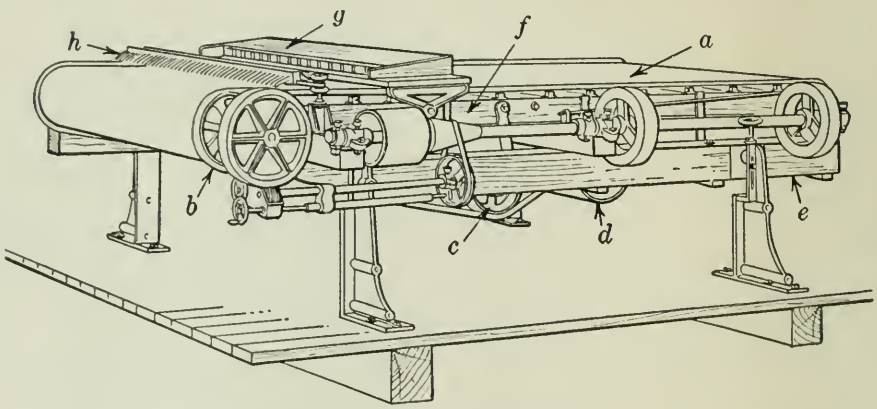

FIG. 61. The Frue vanner

but in the treatment of oxides, carbonates, silicates, etc. the vanner remains the only machine that can handle these fine materials successfully. The Frue vanner is illustrated in Fig. 61. It consists of an endless rubber belt *a* with flanged sides, traveling up a slight incline and around the four drums *b*, *c*, *d*, and *e*. The whole is supported on a frame *f* so constructed that while the belt is moving up the incline it can be given a sidewise shaking motion. The main belt *a* is driven slowly up this incline by means of the head pulley *b*. The pulp is fed upon the belt by a distributing box *g* near the upper end of the vanner. Wash water as required is added over the fingers *h*. The heavy, fine mineral in the feed clings to the belt (it may be either smooth or with corrugations perpendicular to the line of travel), while the coarse, light particles are washed down the incline into the tailings tank. As the belt travels toward the head end the fine mineral, heavy enough to remain on the surface of the belt,

is washed free of light mineral by means of the stream of wash water. This cleaned concentrate finally goes up over the head pulley, where it may be removed into a concentrate tank located under the machine. Some of it drops off by gravity; the rest is removed by a spray of water. The main belt of the Frue vanner is from 4 to 6 feet wide, and the inclined surface about 12 feet long. The speed of the belt, its inclination, and the number of impulses per minute will depend entirely upon the character of the feed and the grade of concentrate desired.

OIL FLOTATION AND OTHER SPECIAL PROCESSES

147. General. The process of oil flotation depends upon the fact that when a mixture of finely crushed sulphide ore and water is strongly agitated with minute quantities of certain oils, and sometimes with acids, alkalies, or salts, a strong froth is formed on the surface of the water. This froth preferentially collects the metallic sulphide minerals and allows the silicates, oxides, carbonates, and other gangue minerals to sink. The separation is often an excellent one, so that the froth may be removed as a concentrate and the gangue rejected as a tailing. Many explanations have been offered, but so far none of them satisfy completely the facts of the case, and they will therefore not be discussed in this text.

148. Oils. Since no satisfactory theory has been evolved to explain the mechanism of oil flotation, we are dependent to a large extent upon experimental work as a means of selecting suitable oils to effect the separation of the different minerals. No one oil or combination of oils can be used on all ores. Each ore is a problem in itself. Although the number of oils which give some flotation effect are almost unlimited, all oils may be divided into frothers and collectors. The frothers are usually light oils, more or less soluble in water, which make large quantities of strong, persistent bubbles when the mixture is violently agitated. This light oil, once the separation is effected, evaporates and allows the froth to break up and free the entrained mineral. Pine oil, pine-tar oil, eucalyptus oil, and hard-wood creosote are examples of effective frothers. The collectors are heavier oils, usually more viscous, insoluble in water, which form a persistent film over the sulphide particles but do not

adhere to the gangue particles. The bubbles of air, or the froth, attach themselves to this film and buoy up the mineral particles. Coal tar, coal-tar creosote, fuel oil, and many synthetic compounds are examples of collectors. It is interesting to note that many of these synthetic compounds are in no sense oils, so that the name *oil flotation* has turned out to be somewhat of a misnomer. Among these compounds are alkaline xanthate, thiocarbanilid, orthotoluidin, and alpha-naphthylamine. Some oils — pine-tar oil, for example — often act as both frothers and collectors, and will give an excellent separation when used alone on an ore. It is important that the oil be well mixed with the pulp before flotation, as free oil seems to kill the froth. The amount of oil necessary to effect a separation will range from as little as $\frac{1}{4}$ pound to as high as 3 pounds per ton of ore treated. It does not seem to be governed by the amount of sulphide present, for the author calls to mind a low-grade silver ore, containing 92 per cent of gangue, which required about 2.3 pounds of oil per ton, and a copper ore, containing only 6 per cent of gangue material, that required but 1.3 pounds per ton. The presence of certain acids, alkalies, and mineral salts often increases the effectiveness of the oils.

149. Differential flotation. It has been pointed out that many of our low-grade ores could not be successfully treated until the development of flotation. Many of our high-grade complex ores could not be profitably worked either. The various ore minerals are present in such a very fine state of division that in order to separate one from the other it is necessary to grind the ore almost to a slime. This slime will not settle rapidly in water and consequently cannot be treated on tables and vanners. By taking advantage of the difference in floatability (see Table XVII) — that is, differential flotation — such complex ores are now being successfully treated. For example, many zinc ores contain, besides the sphalerite, various sulphides of lead, copper, and iron, as well as small amounts of gold and silver. It has been found possible, under certain pulp conditions, to float the lead first, and then, by subsequent flotation under different conditions, to float the other sulphides, one after another. There are many of these processes, and although most of them are as yet imperfect, each year witnesses new and startling developments in this, probably the most important phase

of ore preparation. In general these processes depend upon one of the following methods:

1. The control of the pulp conditions, such as the amount of oil, temperature of the pulp, and length and strength of agitation.

2. A preliminary treatment (for example, roasting) by which one of the sulphides may be filmed over with oxide, leaving the others unaffected. The latter may then be floated from the former.

3. The addition to the pulp of certain chemicals causing one of the sulphide minerals to be floated in preference to another. For example, the addition of copper sulphate or sulphur dioxide has such an effect on lead ores.

TABLE XVII. RELATIVE FLOTABILITY*

Limestone	2.4
Quartzite	5.3
Quartz (SiO_2)	10.7
Sericite	12.7
Calcite ($CaCO_3$)	18.5
Kaolinite ($H_4Al_2Si_2O_9$)	60.0
Pyrite (FeS_2)	62.0
Chalcopyrite ($CuFeS_2$)	66.0
Covellite (CuS)	70.0
Bornite (Cu_5FeS_4)	85.0
Sphalerite (ZnS)	87.0–62.0
Galena (PbS)	92.0
Chalcocite (Cu_2S)	93.0

Method 1 has the disadvantage of delicacy. That is, the difference in floatability between many minerals is very slight under ordinary conditions, so that an attempt to float one in the presence of another by limiting the amount of oil would mean that much of the mineral would find its way into the tailing and be lost. The same may be said of control of temperature and agitation. Method 2 is both expensive and delicate and, with the exception of the Horwood process (involving a preliminary roast), none have been successful.

During the past few years chemists have developed compounds many of which are in no sense oils but have such marked selective properties that the attention of metallurgists is now focused on method 3.

* *Bulletin No. 17*, University of Utah.

150. Effect of chemicals. Owing to lack of space we can indicate only in a very general way the effect of the more common reagents upon the sulphide minerals. For a more comprehensive discussion of this subject the reader is referred to Richards's "Ore Dressing" or Taggart s "Handbook of Ore Dressing." In addition to the flotation agents already described the following are often encountered in differential flotation: (1) lime; (2) sulphuric acid and acid sludge; (3) sodium cyanide; (4) sodium sulphite; (5) sodium silicate; (6) zinc sulphate; (7) copper sulphate.

Lime is commonly used in the flotation of mixed lead-zinc ores. It neutralizes the acid in the feed water, precipitates the soluble sulphates of the heavy metals, and tends to prevent the flotation of the less easily floated sulphides such as pyrite and sphalerite. If present in sufficient quantities it may inhibit the flotation of all sulphides. It is extensively used in the treatment of copper ores to prevent the flotation of pyrite.

At present sulphuric acid and acid sludge are chiefly used for floating pyrite and pyrrhotite that have been temporarily depressed by lime or sodium carbonate.

Sodium cyanide is effective in preventing the flotation of zinc and iron minerals, probably through the formation of cyanides and hydroxides on the surfaces of the minerals.

Sodium sulphite is frequently used to inhibit the flotation of zinc and iron minerals. It is rather drastic in its effects and also has an injurious effect upon subsequent settling.

Sodium silicate tends to promote the formation of a more brittle and consequently cleaner froth.

Zinc sulphate is used a great deal with sodium xanthate and cyanide in the separation of galena from sphalerite. It tends to retard the flotation of zinc and iron minerals.

Copper sulphate has become almost a standard reagent in floating zinc minerals after the removal of the galena.

151. Flotation machines. In general the flotation machines can be divided into those employing mechanical agitation and those employing pneumatic agitation. In the former the pulp is violently agitated by means of propellers, drums, or paddles. By this means minute bubbles of air are beaten into the pulp and distributed uniformly through it, and when the pulp is suddenly led into a quiet chamber an excellent opportunity is

offered for the escaping bubbles of air to attach themselves to the oiled mineral grains. In the pneumatic process the pulp is led over a porous mat, or blanket, up through which air is being forced. This divides the air into minute bubbles, which, rising through the pulp, attach themselves to the oiled sulphide particles and form a froth.

152. The Minerals Separation machine. This was the first commercial machine to be developed and is still one of the

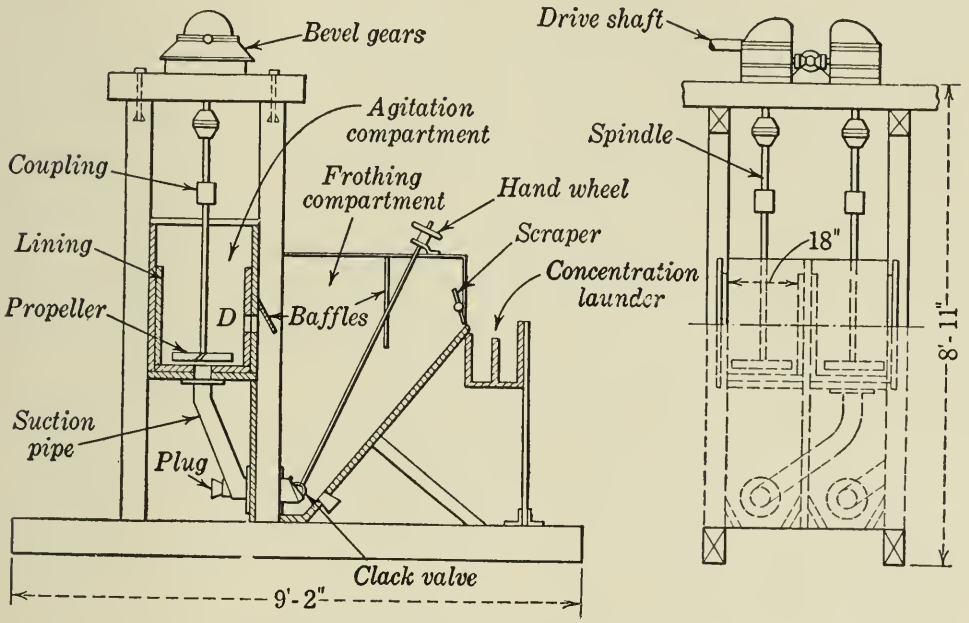

FIG. 62. Minerals Separation machine

most popular. It is of the mechanical-agitation type. It consists of an agitation compartment in which the pulp (consisting of about 4 parts of water and 1 part of ore, the latter crushed to pass about 48 mesh) is violently agitated by means of a propeller driven by a vertical shaft at a peripheral speed of about 1500 feet per minute. In this compartment the pulp is thoroughly aërated and the oil and acid intimately mixed with the charge. The pulp then passes out through the opening *D* into the spitzkasten, or frothing compartment. Here the pulp is quiet, and the sulphide minerals, buoyed up by the bubbles of air, rise to the surface with the froth and can be skimmed off by means of the slowly revolving scraper. The bottom of the frothing compartment is connected with the bottom of the agitating compartment of the next cell in the series by means

of a wooden or metal pipe. The propeller in this compartment acts as a pump, sucking the material from the bottom of the preceding frothing compartment. The rate of transfer, or flow, and hence the level of the pulp in the spitz can be controlled by means of the clack valve. The gangue particles, together with any middling or incompletely oiled sulphides, settle to the bottom of the first frothing compartment, are drawn into the second agitation compartment, are agitated again, and are then floated in the second flotation compartment. The pulp pursues a zigzag course through the machine, being alternately agitated and floated until it is discharged from the last compartment with most of the sulphide mineral removed. A machine with 14 compartments in series, and with propellers 24 inches in diameter, has a capacity of from 400 tons per twenty-four hours on sand to 175 tons on slime. Each cell takes from 5 to 10 horse power. The pulp is usually treated at atmospheric temperature, but it may be heated by means of live steam injected into the first box.

The agitation compartment is subjected to considerable wear, particularly when treating coarse material, so that it is usually lined with wood, as indicated, to protect the frame of the machine. The connecting pipes, propellers, valves, etc. are usually of iron; but if acid is used, or if the water contains $CuSO_4$, it is necessary to make these parts of bronze.

The grade of the concentrate produced is governed partly by the depth of froth in the compartment. In the first two or three compartments a clean concentrate can be produced, running with from 10 to 18 inches of froth. On the next ones, with a smaller depth of froth, concentrates that must be re-treated or middlings that must be reground are produced. The last box usually just overflows and produces a very low-grade middling. Sometimes the whole machine is run as a "rougher," and all the concentrate is re-treated in a second, or "cleaner," machine.

153. The Callow process. This machine is the original of the pneumatic type. A complete installation is shown in Fig. 63. It consists of a rectangular tank *b* about 9 feet long, 2 feet wide, 20 inches deep at the feed end, and 4 feet deep at the tailings end. The inclined bottom of the tank consists of from 6 to 9 air pockets covered with several thicknesses of a loosely woven

canvas twill. This blanket may be reënforced with cocoa matting or perforated metal. Air, at a pressure of 4 to 6 pounds per square inch, is supplied to each of the pockets by the blower *e*. The amount supplied to individual cells may be regulated by the valves so that there is a perfectly even aëration over the entire surface. The air in passing through the blanket is divided into a mass of minute bubbles. These attach themselves to the

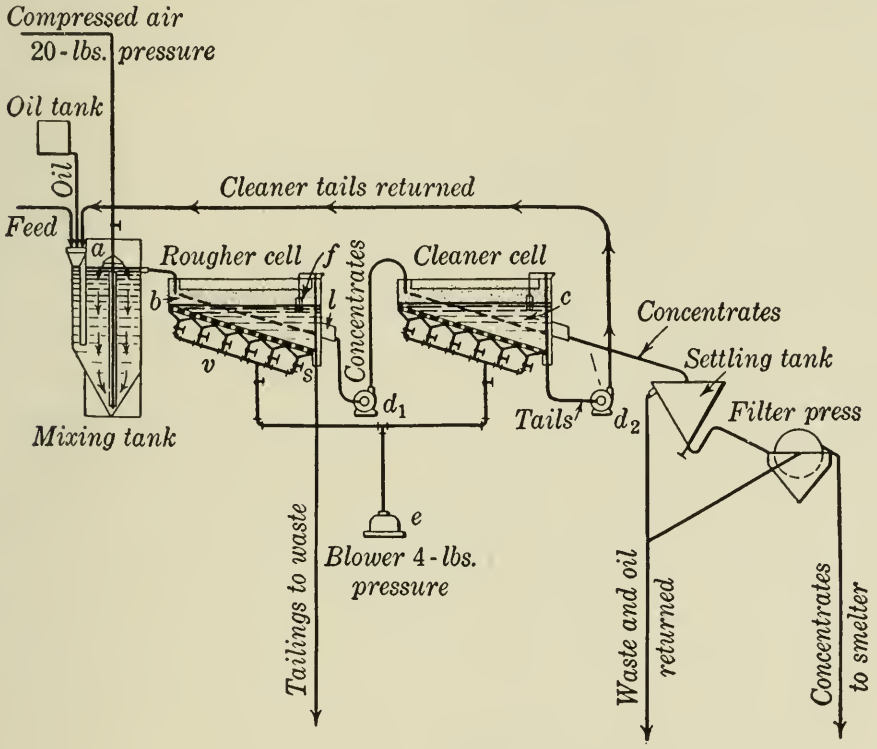

FIG. 63. The Callow flotation unit

mineral particles which have been intimately mixed with the oil and other reagents in a special mixer or in tube or ball mills. These oiled particles rise to the surface as a froth to overflow into a collecting launder *l* which runs along both sides of the machine. The gangue minerals drop to the bottom of the cell and are discharged through the spigot *s*. This is usually fitted with a valve and automatic float *f* so as to maintain any desired depth of froth in the compartment. Usually the mixer *a* can be done away with and most of the oil added to the ball or tube mills.

Each standard Callow cell requires from 3 to 5 horse power and will treat from 30 to 50 tons of ore per twenty-four hours.

The blower must be capable of furnishing at least 10 cubic feet of free air per minute per square foot of porous surface.

As indicated by the illustration, the general procedure is not to make a finished concentrate on one cell but to divide the machines into roughers and cleaners. A rough concentrate is made on the rougher, so that the tailing of the machine will be of sufficiently low grade to go to waste. This rough concentrate is then re-treated on a cleaner, which makes a high-grade concentrate and a tailing that is sent back to the first machine for re-treatment.

154. Oxidized ores. Only sulphide minerals are amenable to flotation; oxides, carbonates, and silicates of the metals sink and join the gangue. Until recent years it was impossible to treat oxidized ores by the flotation process. Today several such processes are being developed. Most of them depend upon the formation of a sulphide film over the other minerals. These artificial sulphides may then be floated in the usual way. One method uses hydrogen sulphide gas; another, sodium sulphide; another, sulphur vapor. On the whole they have not been very successful and have not been applied to large plants, but the process offers a fertile field for investigation.

155. Disposal of flotation concentrate. Table or jig concentrates may be dewatered as we should dewater any granular product, but flotation concentrates are not so easily handled. The froth from the flotation machines contains a large percentage (up to 90 per cent) of water. This froth must be broken up in order to free the mineral, and the water must be removed before the concentrate can be smelted. Many froths break up easily (as soon as the frothing oil evaporates), others drop their mineral load less easily, while still others are very persistent and hard to break up. Very tough froths are to be avoided, since they are a source of trouble about the mill. In general the process of dewatering consists in thickening the concentrate; this gives an overflow of clear water (which, since it contains valuable oil in solution, is sent back to the mill) and a discharge, or spigot, of thickened pulp containing about 45 per cent of water. This thickened material is then sent to a battery of Oliver, Kelly, or American filters, where most of the remaining water is removed and a concentrate with from 9 to 22 per cent moisture is left.

MISCELLANEOUS PROCESSES

156. Magnetic separation. When first developed, magnetic separation was used only with strongly magnetic iron ores. Today, however, with the improvements made possible in powerful electromagnets, it is not necessary that the minerals be strongly magnetic, but merely that they exhibit a *difference* in magnetic susceptibility. Minerals whose specific gravities lie so close together as to prevent efficient water-gravity separation may often be treated by magnetic machines. Such separations as sphalerite from pyrite, rhodonite from garnet, and zincite from calcite are possible. Where it can be used the magnetic separator has proved to be an efficient machine, economical in power, easy of adjustment, and not a source of frequent or expensive repairs. Many machines have appeared on the market, but only a few of these have undoubted merit. For lack of space the author is able to describe only two.

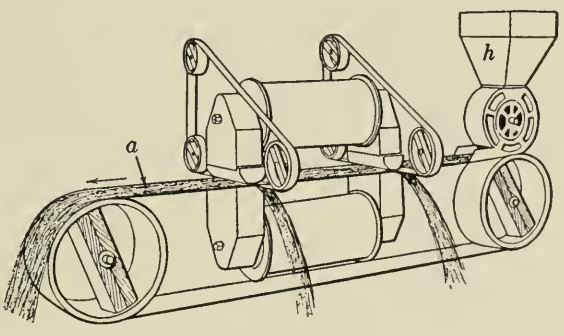

FIG. 64. The Wetherill magnetic machine

157. The Wetherill separator. The principle of operation is shown in Fig. 64. The material to be treated is fed in a thin stream from a hopper *h* onto the main belt *a*, which is from 6 to 18 inches in width. This belt travels in the direction of the arrow at a speed of from 40 to 300 feet per minute, depending upon the character of the ore. This belt passes beneath the poles of a powerful electromagnet as indicated. The poles of the upper magnet have the shape of a sharp wedge; those of the lower are flattened. The cross belts, two in number, serve to keep the magnetic particles from adhering to the poles of the magnets. These take-off belts run at a higher speed than the main belt, so that the magnetic material is thrown off in a stream into receiving bins at the side of the machine. The less magnetic material, which is not attracted by the magnet, passes on and is discharged from the pulley end of the machine. By having several magnets of increasing strength several grades of concentrate may be made.

To energize a large (190,000-turn) magnet will require about 8 horse power, and to drive the mechanism, about 1 horse power more.

158. Dings separator. This machine is of the low-power type and can be used only to treat strongly magnetic materials. It is illustrated in Fig. 65. Ore from hopper *a* is fed in a thin layer upon a vibrating conveyor *b*. This conveyor is given a reciprocating motion by pulley and eccentric *h*, and, since it is inclined

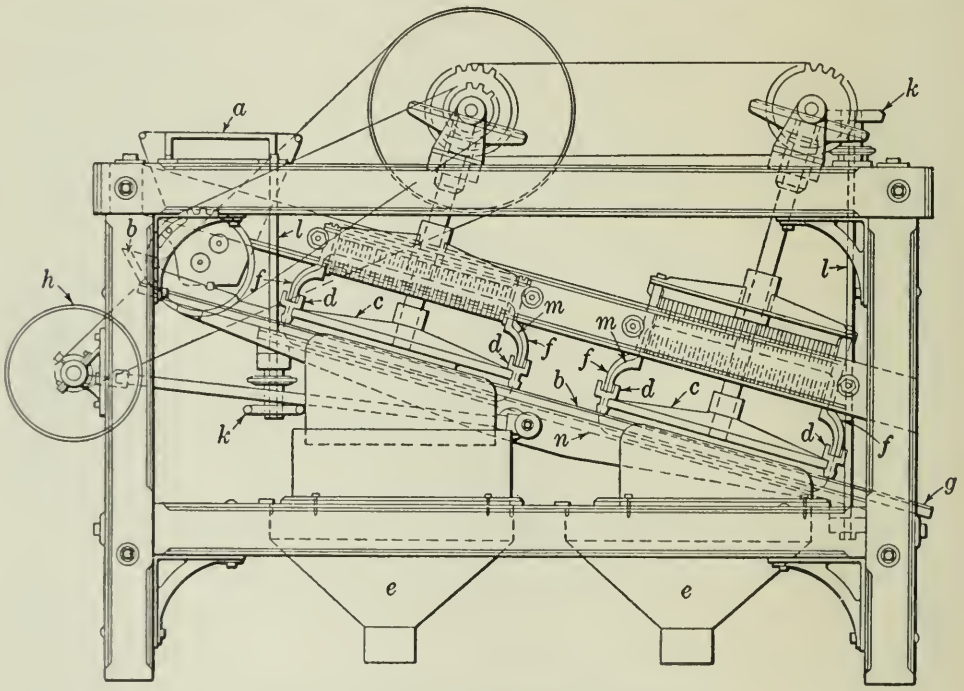

FIG. 65. Dings magnetic machine

slightly, the ore is slowly moved toward the discharge end of the machine. Mounted over this conveyor are two wheels *c* carrying secondary magnets *d*. These are of soft, laminated steel, energized by powerful primary magnets *f*. In their revolution the secondary magnets raise material from the ore stream and carry it out over the edge of the conveyor; but as soon as the magnets are outside the field of influence of the primary magnets, they lose their magnetism and drop their load into the bin *e*. When in their revolution they again cross the belt, they are reënergized, and the cycle is repeated. The nonmagnetic material passes off the end of the tray at *g*.

159. The Huff process. Many metallic sulphides, arsenides, and other minerals are good conductors of electricity, while

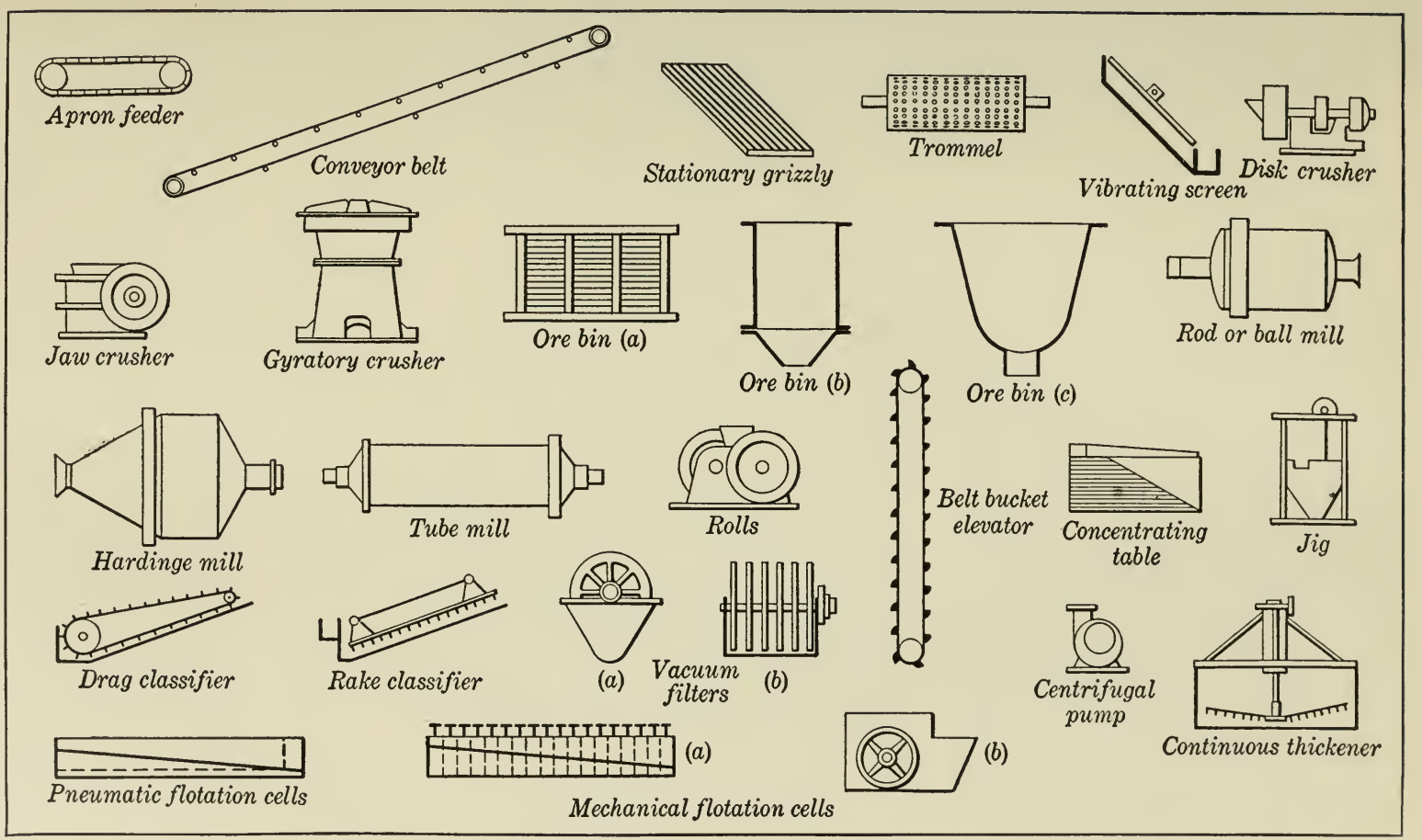

FIG. 66. Symbols used in flow sheets

Courtesy of *Engineering and Mining Journal*

most gangue minerals are poor conductors. Sulphide minerals themselves have different conductivities. This property is taken advantage of in the Huff electrostatic process. The ore (a mixture of good and poor conductors) in a neutral state is fed upon a highly charged revolving drum. The good conductors immediately receive a charge similar to the drum and are repelled.

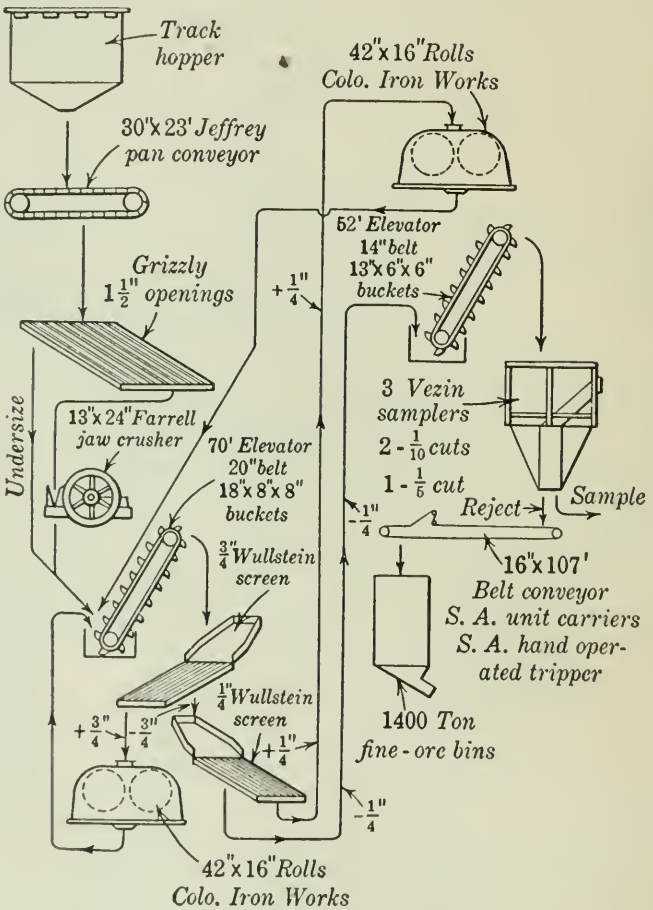

FIG. 67. Flow sheet of a crushing plant

The strength of the repelling action will depend upon their conductivity. Bins are provided at the side of the machine so as to make several products, according to the distance the materials are repelled. The poor conductors are not repelled, but simply slide off the drum into a bin below the machine. The field of this machine is a very narrow one; it is intended for the treatment of ores not amenable to gravity concentration, flotation, or magnetic treatment. The machines so far designed

have small capacities per unit of mill space and are delicate in operation, and the ore must be bone-dry and closely sized.

160. Pneumatic concentration. Air may be used as a concentrating medium in much the same way as water. It is commonly held that a closer separation can be made in air than in water. Air is easily accessible and easily handled, does not freeze, has no chemical action on the ore, and gives a dry product. Air separation, where a finely divided product is desired, as in the preparation of talc, has proved very successful, but air concentration has not been so successful. The Hooper-Paddock jig and the Sutton table are still in the experimental stage. These machines attempt to keep the ore agitated by means of a current of air while stratification by means of jigging or tabling is carried out.

161. Flow sheets. Most metallurgical processes lend themselves well to representation in a diagrammatic form or flow sheet. Some of the symbols ordinarily used in such flow sheets are indicated in Fig. 66. The course of the different products is indicated by lines and arrowheads. Very often, by using different-colored inks or by placing the numerals in circles, squares, or rectangles, we can show on the flow sheet the different tonnages involved, fineness of grinding, water-to-solid ratio, chemical compositions, etc. By this means a process requiring a lengthy description can be easily shown in a simple sketch. A flow sheet of a crushing plant is given in Fig. 67.

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CHAPTER VII

COPPER

162. General. Copper has been known from prehistoric times. The races inhabiting this continent before the Indians lived here knew of and worked this metal. It is widely distributed; there is scarcely a country on the face of the earth but has small deposits of this metal, and next to iron it is the most important. The United States is the chief producing country, accounting for over half of the world's production in 1926.

163. Physical properties. Copper is one of the few metals that occur in the native state, extensive deposits being found in Michigan and Bolivia. The specific gravity of pure copper at 20° C. is 8.89. When pure it is soft. Cast or hard-drawn metal has a tensile strength of from 60,000 to 70,000 pounds per square inch; annealed metal, from 30,000 to 40,000 pounds per square inch. The pure metal is in the highest degree malleable and ductile. It can be rolled into sheets, hammered into foil, and drawn into fine wire. The melting point of pure copper has been established at 1083° C. It is an excellent conductor of electricity, coming next to silver, but small amounts of impurities, especially arsenic and antimony, seriously affect the electrical conductivity. Single crystals ($\frac{3}{4}$ inch in diameter and 14 inches long) have been produced by gradual heating and very slow cooling of copper in an electric furnace. Such crystals have an electrical conductivity 14 per cent greater than that of ordinary copper. So far it has not been possible to take advantage of this property, for such crystals are difficult to produce, and, once deformed, they acquire the properties of ordinary copper, the large crystal breaking up into a mass of smaller ones.

The physical properties of copper fall into two classes,—namely, electrical and mechanical,—and the treatment to attain one has been found to be undesirable for the other. For example, small amounts of Bi, while they interfere seriously with the working of copper, do not affect its electrical conduc-

tivity. A small amount of Cu_2O must be left in the copper in order that it may be in the highest degree malleable. With less than a certain amount of Cu_2O (about 0.4 per cent in ordinary copper), depending upon the other impurities present, it is both hot-short and cold-short; with more than that it is also brittle.

The ductility of copper is improved by hot working, the tensile strength by cold working. In casting, owing to entrained oxygen, the metal formed is likely to be porous and its electrical conductivity low. By adding a little boron just before casting the metal is deoxidized and both the electrical and casting properties improved.

164. Chemical properties. In dry air, or in moist air free from CO_2, copper is not attacked. In moist air or in the presence of CO_2, it becomes coated with a green coating of the basic carbonate. Copper oxidizes readily when heated to a red heat. Copper is readily soluble in HNO_3 and in hot concentrated H_2SO_4.

165. Economic situation. The United States is the largest producer of copper in the world. According to Table XVIII it will be seen that the principal foreign producers are Africa, Chile, Peru, and Mexico. Of late years the American producers have met with serious competition from the South American and African producers. There are immense deposits of high-grade ore in these countries, and with the cheap labor available copper is produced at as low as 6 cents per pound. The question of protecting the domestic producer by a tariff is now being agitated. Electrolytic refineries are located at Baltimore, New York, Great Falls, and Tacoma.

166. Marketing and prices. The copper market is a highly competitive one, particularly in recent years, when the supply has often exceeded the demand. Production and sale of over 90 per cent of the domestic metal is lodged in about fourteen strong companies. Since the World War, when copper fell to a record low of 12 cents per pound, there have been attempts to control the market and artificially stabilize the price, but all these attempts have been failures. The price is governed entirely by supply and demand, fluctuating with conditions in the brass and electrical industry more than with anything else.

There are four grades of domestic copper: electrolytic, lake, arsenical, and casting, or blister. Electrolytic and lake copper

must contain at least 99.88 per cent Cu plus Ag, but they usually contain 99.95 per cent. Arsenical copper must contain at least 99.88 per cent Cu plus Ag plus As, while blister copper may run as low as 99.5. Table XIX gives complete analyses of representative samples.*

The metal is marketed in a number of forms, depending upon the use to which it is to be put. Fully 70 per cent of all the domestic metal is sold in the form of wire bars about 4 inches square and from 3 to 7 feet in length. These are tapered at the end to facilitate their entry into the rolls, and weigh from 125 to 550 pounds. Ingots, the next important shape, are usually in the form of a notched bar weighing from 20 to 25 pounds. Several of these, cast end to end, are termed ingot bars. The price of the red metal over a period of years is given in Table XX.

ORES OF COPPER

The ores of copper fall naturally into three classes: native, oxide, and sulphide.

167. Native copper. The most important deposits of native copper are those found in the Upper Peninsula of Michigan. There the ore averages about 1 per cent Cu, although individual masses of the pure metal have been found up to 100 tons in weight. The ores are concentrated by water-gravity methods to a product containing from 65 to 85 per cent Cu and then smelted in reverberatory furnaces. The copper produced is very pure (99.92 per cent Cu) and usually commands a premium, owing to its higher electrical conductivity. The only other important deposit of native copper is found in Bolivia. On the whole, a very small and decreasing proportion of our domestic copper comes from these native copper ores.

168. Oxide ores. The oxide ores are characteristic of deposits occurring near the surface. They are the result of the alteration and decomposition of primary sulphide minerals by percolating ground waters. These waters, charged with CO_2 and oxygen, act upon the sulphides to produce carbonates, oxides, sulphates, silicates, and various basic salts. This oxidized zone is usually shallow (from 100 to 400 feet in depth). At greater depth the

**Circular 73*, Bureau of Standards.

Table XVIII. World's Production of Copper (expressed in Metric Tons)*

	1910	1915	1920	1921	1922	1923	1924	1925	1926
Africa	7,016	27,327	30,580	38,557	52,816	72,948	104,055	107,213	97,987
Canada	23,810	47,202	35,500	20,532	22,952	36,496	46,274	51,020	58,173
Chile	38,346	52,081	98,952	59,239	129,575	182,384	190,380	190,198	202,319
Mexico	62,504	30,969	45,238	12,316	27,073	54,920	44,589	53,636	56,521
Peru	27,375	32,410	32,982	33,284	36,408	44,166	34,923	37,358	38,740
United States	492,720	646,212	548,418	229,331	431,040	650,912	741,283	759,721	789,082
Bolivia	2,540	3,000	9,900	9,683	9,212	10,654	7,469	6,804	6,441
All others	223,183	255,602	151,607	143,652	157,870	193,240	197,772	228,766	220,200
Total	877,494	1,094,803	953,177	546,594	866,946	1,245,720	1,366,745	1,434,716	1,469,463

* Mineral Industry.

Table XIX. Composition of Commercial Copper

	Lake Wire Bar	Electrolytic Wire Bar	Casting Copper
Cu	99.890	99.893	99.44
Ag	0.0096	0.0020	0.01
Pb	0.0031	0.0072	—
Bi	0.0000	0.0000	0.01
As	0.0062	0.0001	0.02
Sb	0.0000	0.0006	0.05
Se and Te	0.0020	0.0022	—
Fe	0.0028	0.0028	0.38
Ni	0.0090	0.0010	—
Zn	0.0000	0.0000	—
S	0.0016	0.0023	0.002
O (by diff.)	0.0753	0.0888	—

Table XX. Price of Copper (Cents per Pound)

Date	Price	Date	Price
1910	12.74	1923	14.42
1915	17.28	1924	13.02
1917	27.80	1925	14.04
1920	17.46	1926	13.80
1921	12.50	1927	12.92
1922	13.38		

sulphide minerals begin to predominate, until finally the deposit merges into the unaltered primary sulphides. The oxide minerals of copper are as follows:

	Composition	Per Cent Cu
Azurite	$2\ CuCO_3 \cdot Cu(OH)_2$	55.10
Malachite	$CuCO_3 \cdot Cu(OH)_2$	57.27
Chrysocolla	$CuSiO_3 \cdot 2\ H_2O$	36.06
Cuprite	Cu_2O	88.80
Melaconite	CuO	79.84
Brochantite	$CuSO_4 \cdot 3\ Cu(OH)_2$	62.42
Atacamite	$Cu(OH)Cl \cdot Cu(OH)_2$	59.45
Chalcanthite	$CuSO_4 \cdot 5\ H_2O$	25.40

Owing to the ease with which many of these oxide ores can be reduced to the metallic form, such deposits have long since been exhausted.

169. Sulphide ores. These are by far the most important class of copper ores. The large producers of the United States, such as the Utah Copper Company, the Inspiration Copper Company, and the Anaconda Copper Mining Company, are all dependent upon sulphide deposits for the bulk of their ores. As a general rule the oxide ores are quite pure and yield a high-grade copper by simple treatment. The sulphide ores, on the other hand, are highly complex and may contain more than one mineral of copper mixed with sulphides of iron, lead, arsenic, antimony, etc. The smelting of such complex ores is often an expensive and involved process.

The important sulphide minerals are as follows:

	Composition	Per Cent Cu
Chalcopyrite	$CuFeS_2$	34.5
Chalcocite	Cu_2S	79.8
Bornite	Cu_5FeS_4	63.3
Enargite	$3\ Cu_2S \cdot 2\ As_2S_3$	48.0
Covellite	CuS	66.5
Tetrahedrite	$Cu_8Sb_2S_7$	52.06
Tennanite	$Cu_8As_2S_7$	57.0

170. High-grade versus low-grade ores. In the early days of copper smelting it was no uncommon thing — as a matter of fact it was necessary, with the crude appliances and processes then in use — to treat ores running from 10 to 30 per cent Cu.

Such deposits were of course rapidly exhausted, and each generation found itself turning to ores of lower and lower grade. Today any ore containing more than 6 per cent Cu is termed high-grade ore and is usually smelted directly in the blast furnace or reverberatory. An ore with less than 6 per cent Cu is termed a low-grade or milling ore and must be concentrated in order to reject a large part of the gangue, or worthless material, before being smelted. In countries whose natural resources have been but little developed we still find large deposits of high-grade ore. For example, in South America, Africa, China, and Alaska the operators still mine and ship to the smelters in the United States and Europe ores containing 20, 30, and even 50 per cent Cu.

The mineralized areas of the United States have been pretty thoroughly explored; most of our high-grade ores have been located and, thanks to our excellent transportation system, mined, so that today it is not usual to smelt ore direct from the mine. More often than not the ore must be first treated by some concentration process in order to produce a purer and more valuable product. For example, the Utah Copper Company is mining today a copper ore containing about 1 per cent Cu. This is worth, with copper at 13 cents per pound, $2.60 per ton. Smelting costs are seldom less than $5 per ton, so that the treatment of this ore direct would result in a considerable loss. The ore is crushed in order to free the fine particles of copper mineral, which by gravity concentration or oil flotation are separated from the worthless gangue. More than 80 per cent of the copper is thus saved in the form of a concentrate containing from 15 to 30 per cent Cu. The smelting of such a concentrate yields a handsome profit. This company is now treating from 25,000 to 40,000 tons of this low-grade ore each day by this process, — certainly a notable achievement.

At present probably 70 per cent of our copper is produced from such concentrated material. These concentrates range in size from about $\frac{1}{4}$ inch in diameter down to the finest powder. Our smelting practice, therefore, has had to be modified to suit this kind of material, for a furnace smelting lump ore will not work efficiently on such fine material.

171. Uses of copper. The chief use of copper is undoubtedly in the electrical industry. The manufacture of brass, bronze,

and other alloys, sheets, tubing, and castings also consumes very large tonnage. Table XXI gives the estimated average consumption in the different industries in recent years.

TABLE XXI. ESTIMATED AVERAGE YEARLY CONSUMPTION OF COPPER IN THE UNITED STATES (1919–1923)*

	POUNDS	PER CENT TOTAL
Electrical manufactures	302,000,000	28.2
Wire and rods not otherwise included	175,000,000	16.4
Telephones and telegraphs	116,000,000	10.9
Automobiles	132,000,000	12.4
Ships	53,000,000	4.9
Bearings and bushings	63,000,000	5.9
Buildings	65,000,000	6.1
Machine fittings	45,000,000	4.2
Railways	27,000,000	2.5
Ammunition	18,000,000	1.7
Coins	2,000,000	0.2
Fire-extinguishers	4,000,000	0.3
Cash registers	1,000,000	0.1
Miscellaneous	64,000,000	6.0
Total	1,067,000,000	100.0
Manufactured for export	142,000,000	

IMPURITIES IN COPPER

172. Commercial copper. The copper of commerce is never pure. As indicated by the analyses in Table XIX, the total amount of impurities may be small, but even the presence of a small amount of a single element may seriously impair the physical properties of the metal. The presence of two foreign elements may be additive, they may neutralize each other, or they may act independently and interfere with each other.

173. Oxygen. It is fairly well established that oxygen is insoluble in copper. All the oxygen is present as Cu_2O, which is the only oxide stable at the melting point of the metal. *Set*, or *dry*, copper (metal saturated with Cu_2O) contains about 6 per cent Cu_2O, while *tough-pitch* copper contains about 0.4 per cent, the amount depending upon the other impurities present. The tensile strength of copper begins to be affected by 0.45 per cent Cu_2O. The malleability begins to decrease at 0.9 per cent Cu_2O.

* Spurr and Wormser, Marketing of Metals and Minerals.

174. Lead. The amount of lead ordinarily found in commercial copper is too small seriously to affect its physical properties. Ordinarily 0.15 per cent Pb in copper will not affect the malleability or tensile strength. The effect of Pb is influenced by the other impurities present. For example, oxygen-free copper with 0.05 per cent Pb is red-short; oxygen-bearing copper with as much as 0.2 per cent Pb can be readily worked either hot or cold.

175. Bismuth. This is considered the most objectionable impurity in copper. As little as 0.025 per cent makes copper hot-short, 0.05 per cent makes it cold-short, and 0.1 per cent renders it very brittle. The presence of As and Sb tends to counteract this bad effect.

176. Iron. Iron is always likely to be present in commercial copper, but usually not in harmful amounts. It tends to make the metal both hard and brittle.

177. Arsenic. Arsenic present in as large amounts as 0.4 per cent does not affect the mechanical properties of copper, but it does increase the electrical resistance. With larger amounts it begins to produce red-shortness. Generally 0.6 per cent is considered the limit for good copper.

178. Antimony. The effect of Sb is somewhat similar to that of As. The limit for good copper is generally looked upon as 0.05 per cent. Up to 0.5 per cent it increases the tensile strength of copper and does not interfere with the malleability, although it does affect the ductility.

179. Other impurities. Sulphur, iron, tin, and zinc should never be present in refined copper. Phosphorus is sometimes added in order to produce sound castings, but it has a bad effect on the electrical conductivity. Silicon in small amounts increases the tensile strength without affecting its malleability or ductility.

180. Industrial alloys. The alloys of copper are in general more fusible and more fluid than copper; they give sounder castings and are harder, less malleable, and less corrodible. The leading alloys of copper are those with Zn, Sn, and Al. The alloys with Zn are called *brasses*, and those with Sn *bronzes*. Table XXII gives analyses and melting points of typical alloys of copper.

TABLE XXII. INDUSTRIAL ALLOYS OF COPPER

	Cu	Zn	Sn	P	MELTING POINT IN DEGREES CENTIGRADE	COLOR
Red brass	90	10			970	Yellow-red
Fine casting brass .	80	20				Yellow
Fine yellow brass .	70	30				Pale yellow
Standard yellow brass	66.6	33.4			895	Deep yellow
Muntz metal . . .	60	40				Golden yellow
White brass	35	65				Silver gray
Malleable bronze .	98–94		2–6			Red to reddish yellow
Gun metal	92–88		8–12			Reddish yellow
Phosphor bronze . .	90–91		9–8	< 1		Reddish yellow
Silicon bronze . . .	88		10	2		White

EXTRACTION OF COPPER FROM ITS ORES

181. General. Copper may be extracted from its ores by the dry, or smelting, method, on the one hand, or by the wet, or leaching, method, on the other. In the first case the entire mass of ore, together with coke and suitable fluxes, is raised to a fusion temperature in order to produce a matte, or enriched mixture of iron and copper sulphides. This matte is then reduced to metallic copper in a converter. In the wet method the ore is crushed, in order to present a large surface, and then acted upon by suitable solvents. These dissolve the copper but leave unaffected the base metals and the gangue. The dissolved copper can then be precipitated and recovered.

182. Dry, or pyrometallurgical, methods. Although hydrometallurgical methods for the extraction of copper are gaining in popularity every year, it is safe to say that fully 90 per cent of the world's copper is still produced by smelting. As indicated below, the method of treatment will depend entirely on the physical and chemical characteristics of the ore.

Oxidized ores such as malachite, azurite, cuprite, and native copper ores may be reduced in the blast furnace directly to black, or impure, copper with comparative ease. The charge consists of ore, coke, and flux. The coke supplies the heat necessary to raise the temperature of the mass to a point where the chemical reactions of reduction may go on. The flux unites with the iron and other base oxides as well as with the gangue to form

a fusible slag. The carbon of the coke, together with the CO formed by incomplete combustion, reduces the oxides of copper to the metal. The black copper and slag separate readily, owing to differences in specific gravity and to the fact that they are insoluble in one another.

The smelting process with sulphide ores is also carried out in a blast furnace, but the principles involved are quite different. The charge is made up of raw or roasted ore, coke, and flux. As before, the coke supplies the heat and the flux unites with the gangue of the ore to form a fusible slag. Sulphur acts partly as a fuel and in burning to SO_2 furnishes heat for the other reactions. In fact, in pyritic smelting, with ores rich in sulphur, no coke is added and the sulphur furnishes all the heat. Pyritic methods have not been generally successful. The copper sulphide and iron sulphide dissolve in each other to form a matte which is insoluble in the slag and has a higher specific gravity. Separation of the two is easily effected. The matte also has the property of dissolving any gold or silver occurring in the ore. The copper in a 6 per cent ore may thus be concentrated into a matte containing 40 per cent Cu. This matte can then be reduced to metallic copper in a converter and further refined, if necessary, by fire or electrolysis.

183. Wet, or hydrometallurgical, methods. In these processes the ore (usually roasted) is acted upon by a solvent such as H_2SO_4, HCl, or $Fe_2(SO_4)_3$. Dilute solutions of these reagents dissolve the copper compounds and leave unattacked the rock minerals of the gangue and most of the base metal oxides. The insoluble material can be separated from the copper solution by filtration or decantation, and the solution purified and the copper recovered by chemical or electrical precipitation. It has the obvious advantage that only a small part of the ore enters into the chemical reaction.

THE BLAST FURNACE

184. Hearth. A Great Falls, or Klepetko, blast furnace is shown in Figs. 68A and 68B. Since a blast furnace of this description, with its charge of ore and fuel, weighs sometimes several hundred tons, the foundations must be massive and secure. The slightest settling after operation has started would crack the water

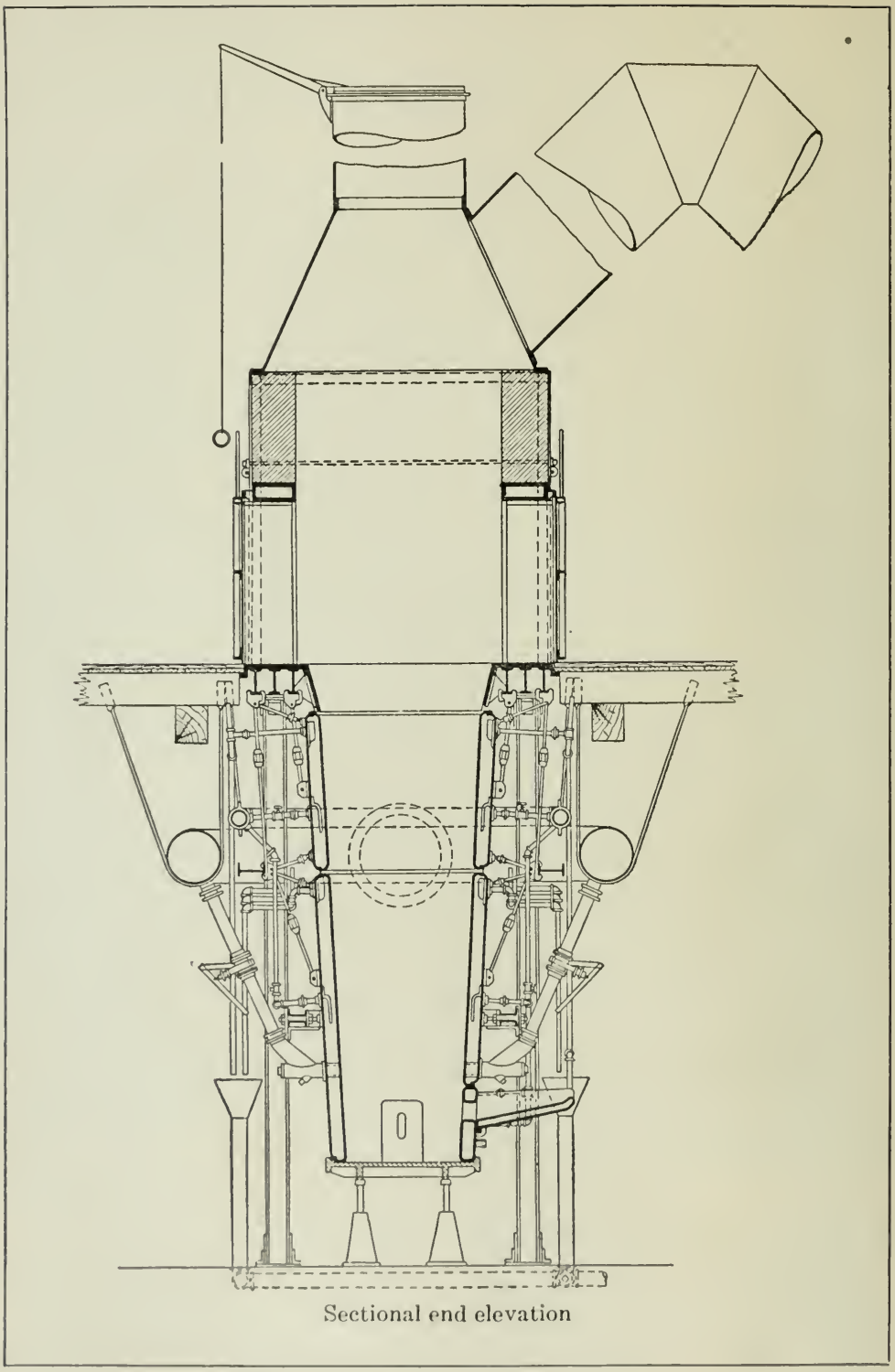
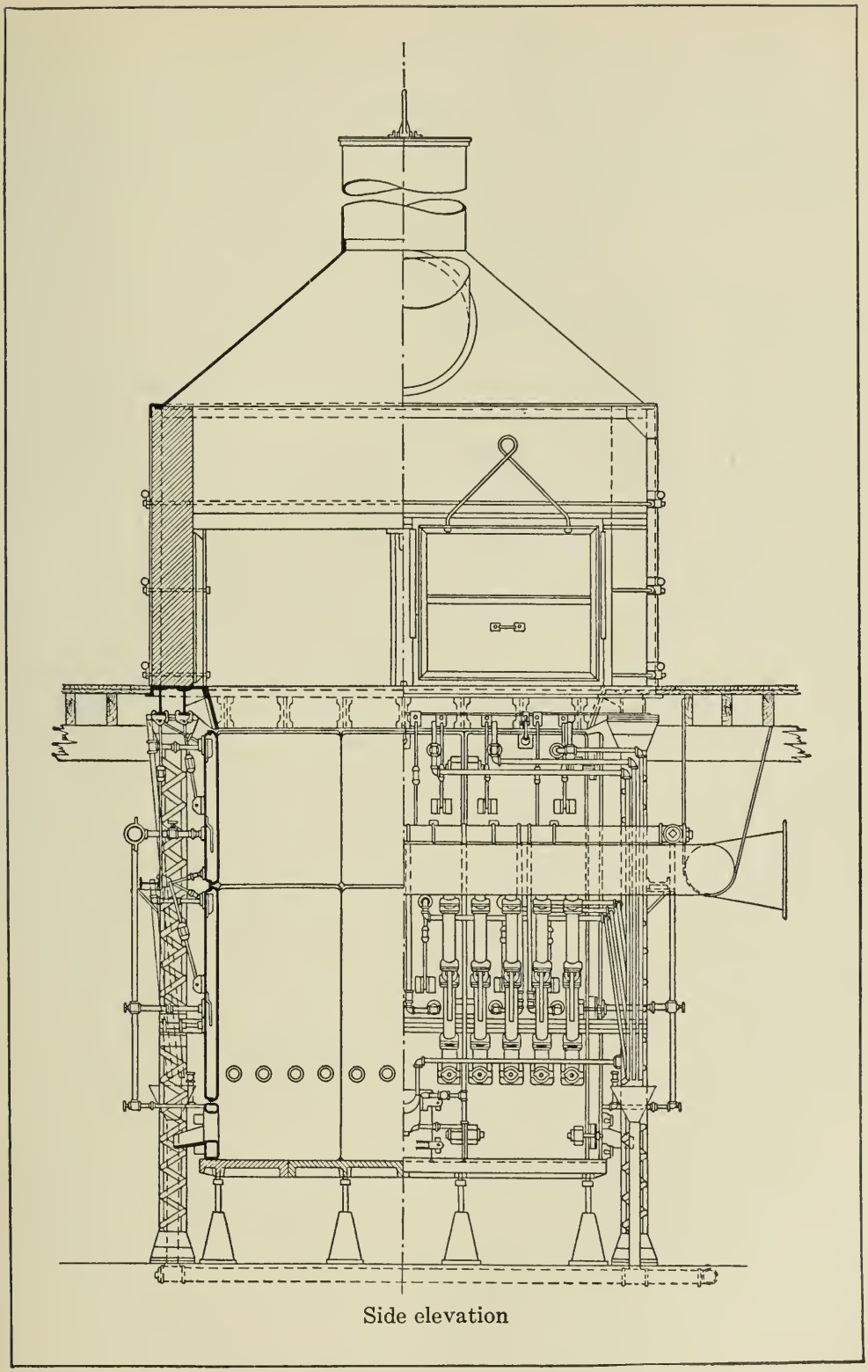


FIG. 68A. A copper blast furnace



Side elevation

FIG. 68B. A copper blast furnace

jackets and do irreparable damage to the structure. The hearth and crucible (which holds the molten material) is usually built up solid from the concrete foundations. Most metallurgists use the highest grade of fire brick, but in recent years a few hearths have been built from the more refractory chrome or silica brick.

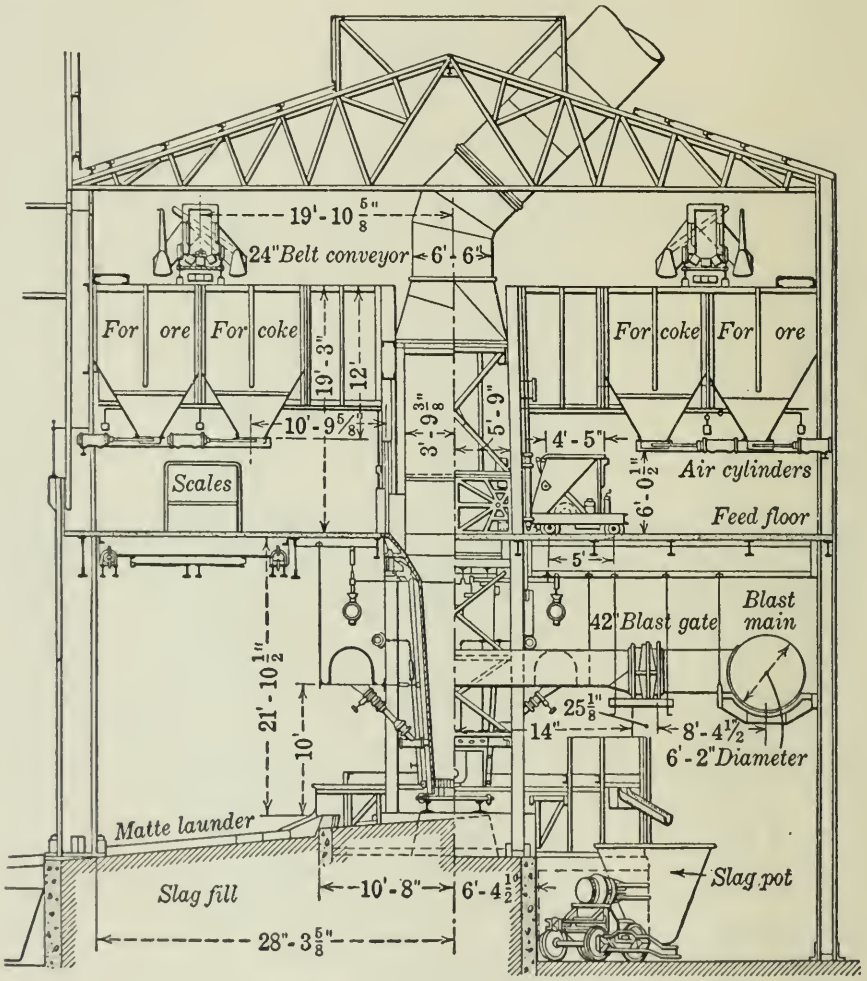


FIG. 69. A blast-furnace plant

The latter are not corroded so easily by mattes low in copper. Chrome brick, however, has the undesirable property of absorbing large quantities of matte, and the copper thus absorbed is difficult to recover. The *trapped spout* for the continuous overflow of matte and slag is located at the center of one side or sometimes at both ends of the furnace. Before material can overflow, it must fill the spout and cover the outlet or tap hole. Thus it prevents the escape of the blast, and the slag and matte

flow out in a regular stream as fast as formed in the furnace. A tap hole, indicated on the left of the front elevation, must be provided for completely draining the crucible when the furnace is shut down for repairs. The bottom of the hearth, in case the spout is in the center, slopes from the ends toward this center in order to promote the collection and flow of the matte. The discharge spout often has a water-cooled jacket.

185. Shaft. In cross section the shafts of American blast furnaces for the treatment of copper ores are usually oblong, although small matting furnaces may be circular. The working height, or smelting column, is from 10 to 14 feet. The shaft is built of jackets made of steel plate, through which water circulates. The inner, or fire, plate is $\frac{1}{2}$ inch to $\frac{7}{8}$ inch in thickness, and the outer plate about $\frac{3}{8}$ inch. Formerly the plates were riveted, but trouble through corrosion of these rivets, and the rapid development of welding, have resulted in the employment of the latter method in the more modern furnaces. These water jackets are pierced, as indicated, by tuyère holes for the insertion of the tuyère pipe. In the case of the larger furnaces the jackets are divided vertically into two sections; this facilitates removal for repairs, besides making the repairs less expensive. The jackets are braced by longitudinal I beams and tie-rods, are firmly bolted to the hearth below, and are also carried on the I beams forming the superstructure of the entire furnace.

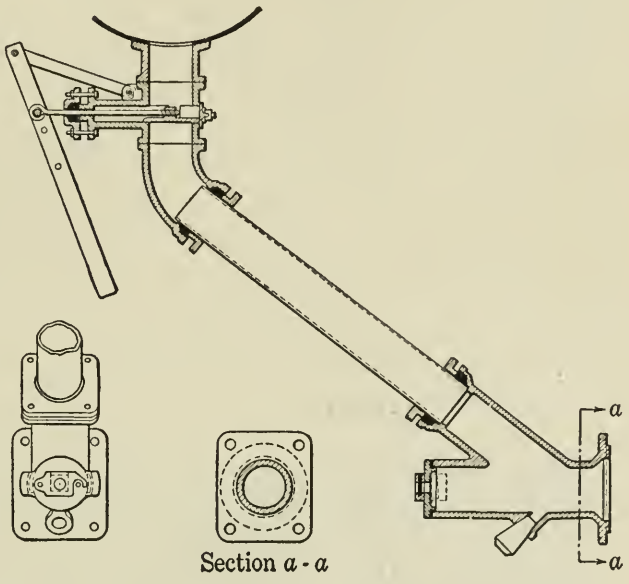


FIG. 70. The tuyère of a copper blast furnace

The width of the shaft at the tuyère level varies from 42 to 56 inches, and the length from 150 to 1100 inches. The tendency, in recent years, has been to increase the size of copper-matting furnaces. Increase in width would require higher blast pressure to drive the air to the center of the furnace, and it is

doubtful if the larger furnaces would be as efficient as the smaller ones. Increased capacity is best gained by increasing the length of the furnace. The advantages of very long furnaces such as are used at the smelter of the Anaconda Copper Mining Company are a saving in the cost of the end jackets, a smaller loss of heat through radiation, lower fuel consumption, and regular and more efficient smelting.

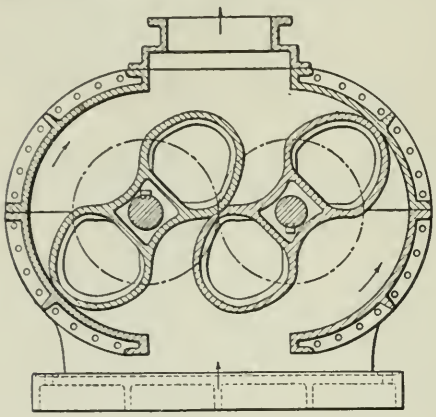


FIG. 71. A rotary blower

186. Tuyères. The tuyères are located a few inches above the top of the crucible. They are pipes, often water-cooled, through which air under pressure is admitted to the furnace. They are usually circular in cross section and from 2 to 5 inches in diameter. They are spaced from 10 to 18 inches, center to center, and are connected with the *bustle pipe*, which brings air (at a pressure of from $\frac{1}{4}$ pound to 2 pounds per square inch) to

FIG. 72. A Roots-blower installation

the furnace. This air is supplied by a rotary blower shown in Figs. 71 and 72. Where the inclined part of the connecting pipe meets the horizontal tuyère there is a hole through which the conditions at the focus of the tuyère can be observed and

through which a rod can be inserted for clearing the tuyère pipe in case it becomes clogged with congealed matte or slag. This bustle pipe is made of steel plate and is from 12 to 20 inches in diameter.

187. Charging floor. The charging floor is located at the upper limit of the shaft. Small furnaces may be charged by hand, but large furnaces are fed from cars (shown in Fig. 73) which run upon tracks on each side of the shaft opening. Charges can then be fed from either side in order to keep the top of the smelting column even and in proper condition. Furnaces are run with either open or closed top. If the latter, the opening is closed by means of counterbalanced sheet-iron doors when the furnace is not being charged. A section of a typical blast-furnace plant is shown in Fig. 69.

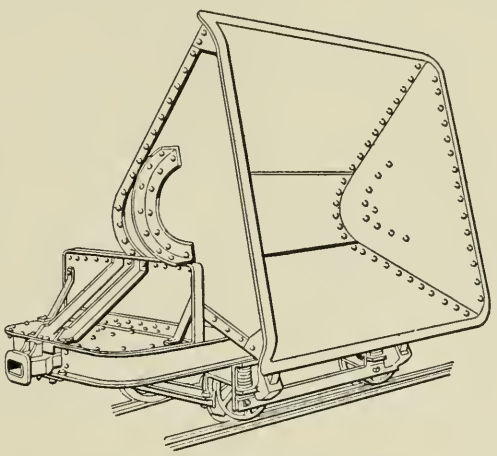


FIG. 73. A charge car

188. Withdrawal of gases. This is carried out by means of a gooseneck, or sheet-iron flue, connected with the brick superstructure of the furnace. The gooseneck varies in size from 4 to 9 feet in diameter, according to the volume of gases produced. This flue carries away the products of combustion and fine particles of ore which are blown out of the furnace. These gases are afterward cooled, their velocity is checked, and this material is recovered for treatment, since it contains considerable quantities of copper, silver, arsenic, and antimony.

189. Capacity. The furnace indicated in Fig. 68 has a capacity of about 350 tons of charge per twenty-four hours, or about 5 tons per square foot of hearth area. At the Anaconda plant, by joining together adjacent furnaces until the combined length was over 80 feet, it was found possible to smelt 2500 tons per twenty-four hours, or 6 tons per square foot of hearth area, and this with a smaller percentage of coke in the charge.

190. Settler, or forehearth. This is a fire-brick-lined container placed in front of the furnace for the collection of the slag and matte as it issues from the spout. In it the separation of the

matte and slag takes place. The specific gravity of the matte varies from 4.8 to 5.4, while that of the slag averages about 3.6. In small plants these settlers are portable, running upon a small track in front of the furnace. They have the advantage of being easily removed for repairs. In the larger plants, however, they are of the stationary type indicated in Fig. 74. Such large settlers are from 6 to 20 feet in diameter and from 3 to 5 feet in depth. They are built of boiler plate and lined on the sides and bottom with basic brick to resist the corrosion of the slag. The mixture of slag or matte enters the settler at *a*, and the matte, owing to its high specific gravity, settles to the bottom and can be removed through the tap hole. From 5 to 10 tons are withdrawn as required for treatment in the converter. When this operation is completed, the tap hole may be closed by a plug of fire clay. The slag overflows continuously from the slag spout on the opposite side of the settler from *a*.

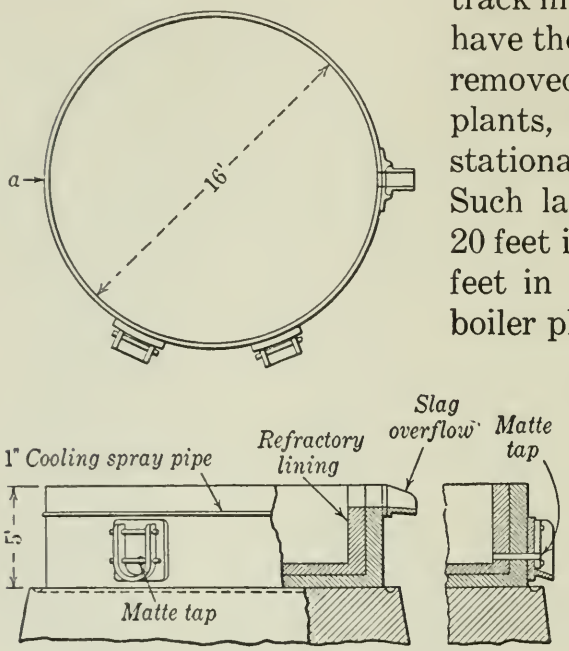


FIG. 74. A settler, or forehearth

ROASTING OF COPPER ORES

191. General. Most copper ores are best treated after roasting. The object of roasting is to eliminate a part of the S and as much of the As, Sb, and Bi as possible, and to oxidize the iron sulphide so that it will readily unite with the flux to form a fusible slag. Nearly all copper ores which are to be smelted in the reverberatory furnace must be roasted first. The degree of this roasting will depend upon the percentages of S, Cu, and Fe present in the ore. In blast-furnace smelting the preliminary roast is not so important, but in the reverberatory smelting of sulphide ores the degree of concentration is almost directly proportional to the elimination of S. On the whole, roasting

is a troublesome operation, requires complicated and expensive apparatus, and is costly to operate. The metallurgist seeks to avoid it when he can.

192. Chemistry. Let us assume that the ore to be roasted consists of the minerals chalcocite (Cu_2S), chalcopyrite ($CuFeS_2$), pyrite (FeS_2), and gangue. Let us further assume that this ore has been crushed so that it is in the pulverulent form encountered in most concentrates. When this ore is heated with an excess of air, the gangue, unless it is a carbonate, will be unaffected at the temperature prevailing.

Chalcocite ignites at a temperature of from 430° to 697° C., depending upon the size of the particles, and is oxidized as indicated below:

$$Cu_2S + 3\,O = Cu_2O + SO_2,$$
$$Cu_2O + SO_2 + O_2 = 2\,CuO + SO_3,$$
$$CuO + SO_3 = CuSO_4.$$

The proportions of oxide and sulphate formed will depend upon the temperature of the roast and upon the amount of air admitted.

Pyrrhotite is a common constituent of sulphide copper ores. When roasted it first loses an atom of S. Then, at a temperature of from 380° to 530° C., the following reactions go on:

$$FeS + 3\,O = FeO + SO_2,$$
$$3\,FeO + O = Fe_3O_4,$$
$$SO_2 + O + \text{catalyst} = SO_3,$$
$$FeO + SO_3 = FeSO_4.$$

Again the relative proportions of oxide and sulphate from the reactions above will depend upon the conditions in the furnace. The $FeSO_4$ formed will be broken up when heated above 530° C.

Chalcopyrite is really a solid solution of Cu_2S in pyrrhotite, and therefore behaves like pyrrhotite.

Pyrite, if heated with the exclusion of air, begins to give off its sulphur at 200° C. according to the reaction

$$2\,FeS_2 + \text{heat} = 2\,FeS + S_2.$$

If further heated in air it begins to give off SO_2 at a temperature of from 260° C. to 300° C., and the following reactions take place:

$$4\,FeS_2 + 11\,O_2 = 2\,Fe_2O_3 + 8\,SO_2,$$
$$FeS_2 + 3\,O_2 = FeSO_4 + SO_2.$$

193. Apparatus. At plants where the tonnage is too small to warrant an expensive roasting installation, or where labor is cheap, lump ore may be profitably roasted in heaps or stalls. In

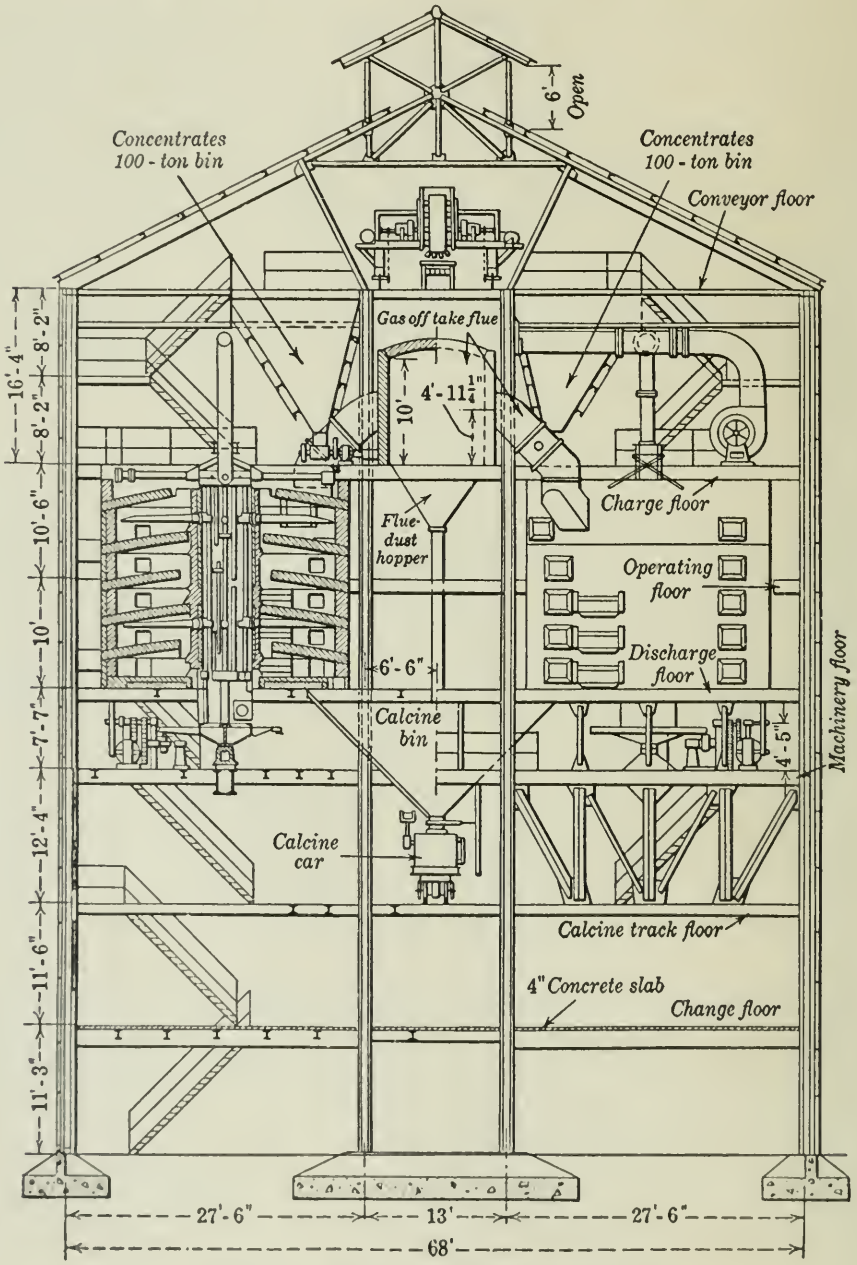


FIG. 75. A Wedge roasting plant

all modern plants, however, the roasting is carried out in some type of mechanical roaster already described in Chapter IV. The choice of the furnace to be used will depend upon the chemical composition of the ore, its physical condition, the time

that can be given to roasting, the value of the ore, and whether or not the gases produced are to be utilized in the manufacture of sulphuric acid. In modern smelters multiple-hearth furnaces of the Wedge or the MacDougall type are almost universally used. Where extraneous heat has to be applied for the roasting operation the gases from such furnaces are mixed with excess air as well as with the products of combustion, and therefore cannot be used for the manufacture of sulphuric acid.

194. Capacity of furnaces. A seven-hearth Wedge with a drier, or preheating hearth, 23 feet in diameter, with an effective hearth area of 1940 square feet (exclusive of drier hearth and drop holes), is rated at a capacity of 70 tons of sulphide copper ore per 24 hours. The original ore, which contains 35 per cent S, is reduced to 7 per cent S in the roasting operation. By crowding, such a furnace can be made to treat as high as 100 tons per 24 hours, but such roasting is imperfect. Auxiliary heat may be furnished by oil-burners or outside fire boxes in case the combustion of the sulphur is not sufficient to keep the furnace at the ignition temperature of the sulphides.

195. Costs. Naturally these vary widely according to the physical character of the ore and the degree of elimination of sulphur. Furnaces of the Wedge and the MacDougall type can roast sulphide copper ore from 35 per cent S down to 7 per cent S at a cost of about 50 cents per ton treated. Reverberatory hand roasting may go as high as $2 per ton.

SMELTING OF OXIDE COPPER ORES

196. General. The smelting of oxide copper ores in the blast furnace is a relatively simple operation and has the advantage that the copper is obtained in the metallic form, although impure, in one operation. This black copper, as it is called, contains from 95 to 98 per cent Cu. The principal impurities are S, As, Sb, Ag, Au, and Fe. Such copper of course cannot be used directly in industry. The ore, which must contain but little sulphide, is charged into a blast furnace, similar to the one just described, and smelted down with coke and a suitable flux. Cuprite is reduced by C and CO according to the following reactions:

$$2\,Cu_2O + C = 4\,Cu + CO_2,$$
$$Cu_2O + CO = 2\,Cu + CO_2.$$

Any malachite or azurite is dehydrated in the upper levels of the furnace and similarly reduced. The gangue of the ore, if it is siliceous, unites with the CaO of the flux and the FeO of the ore to form a fusible calcium-iron silicate (the slag).

In the crucible of the furnace is collected the molten slag and copper, the former, because of its lower specific gravity, floating on top. Ordinarily the slag does not overflow continuously as in the ordinary blast furnace. Instead of one trapped spout, as in the furnace illustrated in Fig. 68, there are two tap holes. The lower one, close to the bottom of the crucible, is for the copper, while the upper one, a few inches higher, serves for the slag. When these accumulate in the crucible they can be removed by breaking the clay plug which closes the tap hole. The slag is received in a forehearth immediately in front of the furnace. This slag contains small drops of metallic copper which have not had time to settle through the slag in the furnace. A part of this copper is recovered in the forehearth, but the loss of copper in the slags is much higher than in matte smelting. The copper accumulates in the crucible of the furnace and is removed from time to time and cast into ingots for shipment to the refinery.

Oxide copper smelting has been given up in this country because the small amount of such ore now available can be better smelted along with sulphide ores. The Union Minière du Haut Katanga, at its mines in Africa, has an enormous deposit of oxidized ore. The ore averages about 6 per cent Cu, although some of it runs 20 per cent or more. The furnaces used are large (for oxide furnaces), being 44 inches by 240 inches. The slag overflows continuously from one end of the furnace. The slags from the smelting of oxide copper ores, owing partly to the high grade of the ores and partly to the fact that the copper does not settle as readily through the slag as does a matte, are higher in copper than those produced in matte smelting. They average about 0.7 per cent Cu and often run over 1 per cent.

SMELTING OF SULPHIDE ORES

197. General. From a metallurgical standpoint a sulphide copper ore consists of Cu_2S, FeS, and gangue. The separation of the copper from the iron and the base metals of the gangue is based upon the following facts:

1. That copper has a stronger affinity for S than has iron.
2. That iron has a stronger affinity for O than has copper.
3. That Cu_2S and FeS dissolve in each other to form a matte.
4. That this matte has a higher specific gravity than the slag and is insoluble in it.
5. That this matte possesses the power of dissolving the gold and silver contained in the original ore.
6. That Cu_2S and Cu_2O will react with each other when heated to 450° C. to form metallic copper and SO_2. This is the reaction involved in the "converting" of the matte in a Bessemer converter.

Blast-furnace smelting is carried on by three different processes:

1. The roasting and reduction process, in which the partially roasted ore is smelted in a blast furnace with a large percentage of coke, which furnishes the heat and reduces the oxides of copper.
2. The pyritic process, which utilizes the heat produced in the oxidation of the sulphur. The sulphur of the charge in burning to SO_2 and the formation of a ferrous silicate generate sufficient heat to allow the reactions of slagging and matting to go on.
3. The partial pyritic process, in which, as the name indicates, only enough coke is added to make up the heat deficiency and keep the furnace at the proper temperature.

It may be mentioned in passing that strictly pyritic smelting, while very desirable from an economic standpoint, has never been very successful. The process is delicate, and slight irregularities in operation cause trouble. In the United States, even in what is called pyritic smelting, it is usual to add a little coke (about 3 per cent of the weight of the charge) to promote better working of the furnace.

198. Copper matte. Matte is a complex mixture of Cu_2S and FeS, and in practice varies from 15 to 60 per cent Cu. If an ore containing oxides and sulphides of copper, iron, and other base metals, together with gangue, is melted down, it will be found that the copper will unite with the sulphur. Any sulphur over and above the amount necessary to combine with the copper will unite with the iron, and these two sulphides will dissolve in one another to form a matte. If lead or nickel is present in the charge, that also will enter the matte as a

sulphide. As, Sb, and Bi are only partly eliminated in the preliminary roasting operation and in the blast furnace. Whatever of these elements remains in the ore also joins the matte. The matte serves as an efficient collector of both the silver and the gold. The following table shows the range in composition of the matte:

	Cu	S	Fe	Ni	Specific Gravity
	Per Cent	*Per Cent*	*Per Cent*	*Per Cent*	
Reverberatory furnace (Anaconda)	60.8	23.3	11.4	—	5.4
Blast furnace (Butte)	36.2	23.4	25.0	—	5.1
Blast furnace (Jerome, Arizona) .	55.0	24.0	13.9	—	5.3
Blast furnace (Sudbury, Ontario) .	24.5	23.2	28.7	15.6	5.1

The melting point of a matte increases with the per cent of copper as indicated below:

Per Cent of Cu	Melting Point in Degrees Centigrade
32	875
50	955
60	1065
70	1120

199. Copper slags. The slags formed in the smelting of copper ores in both the blast furnace and the reverberatory furnace vary from the subsilicate to the bisilicate. Such a variation is possible, for the only conditions to be satisfied are that the slag be fluid enough to flow readily from the tap hole and of such a specific gravity as to promote the separation of the matte from the slag. The following table indicates the variation in practice:

	Per Cent
SiO_2	28–40
FeO	2–60
Al_2O_3	2–18
CaO	2–20
MgO	0–8
ZnO	0–20
BaO	0–20

MgO, ZnO, and BaO are undesirable, since they give rise to pasty, viscous slags. The refractoriness of many ores is due to the presence of these compounds. High iron tends to give a slag of too great a specific gravity, while high silica gives viscous

slags. Cu_2S is slightly soluble in siliceous slags, and it has been found that this solubility falls with the silicate degree and with the replacement of FeO by CaO. In general, slags which contain a metal having much affinity for S will carry more Cu than those containing a metal with less affinity for S.

REDUCING SMELTING

200. General. In this process the ore is first rough-roasted, and then smelted in the blast furnace with sufficient carbonaceous fuel to furnish the necessary heat and reduction. The blast should oxidize only the C and none of the S. A small amount of sulphur may be burned, but most of the SO_2 in the waste gases from the furnace is derived from the reactions between the sulphides and oxides of copper as indicated below. The Cu, Fe, and S unite to form a matte, and this absorbs, besides the precious metals of the ore, a large part of the As, Sb, Zn, and Pb. The SiO_2, FeO, and CaO of the gangue unite with the necessary fluxes to form a fusible silicate, or slag.

The fuel ordinarily used is coke, to the amount of about 16 per cent by weight of the charge. Charcoal may be used, but it lacks the mechanical strength of coke. It is better to have too much than too little coke, for a slight drop in the temperature of the furnace often detracts considerably from its smelting capacity.

201. Chemistry. As the ore descends in the shaft of the blast furnace the water is driven off from the hydrated minerals. Any CuO present will be reduced and sulphurized:

$$CuO + CO = Cu + CO_2,$$
$$2\,Cu + FeS = Cu_2S + Fe.$$

Fe_2O_3 will be reduced by both C and CO, and the FeO thus formed will unite with the silica of the charge to form a slag:

$$Fe_2O_3 + CO = 2\,FeO + CO_2,$$
$$FeO + SiO_2 = FeSiO_3 \text{ (slag)}.$$

The reduction and sulphurization go on as the charge sinks in the furnace. Copper oxide and copper sulphide react to produce metallic copper and SO_2 with a corresponding elimination of sulphur:

$$2\,Cu_2O + Cu_2S = 6\,Cu + SO_2.$$

This copper is immediately sulphurized by any pyrite present:

$$2\,Cu + FeS = Cu_2S + Fe.$$

If there is not enough sulphur present to take care of the copper and iron in this way, there is danger of loss of copper in the slag through the formation of a silicate. The matte begins to form at a temperature of about 900° C. and trickles down over the white-hot pieces of flux and ore, absorbing the precious metals. Slag formation begins a short distance above the tuyères. Sulphates will be decomposed thus,

$$MSO_4 + \text{heat} = MO + SO_3,$$

and the resulting oxide reduced and sulphurized. The temperature at the tuyères is about 1200° C., and decreases gradually to 250° C. or higher at the mouth of the furnace.

Now as to the changes which take place in the ascending gas current. The blast entering the tuyères strikes coke at a temperature of 1200° C. This burns to CO, and a small amount of this (if there is excess air) burns to CO_2, so that just above the tuyère level the gas consists of CO, CO_2, and N. There is a tendency for the C to reduce the CO_2 to CO, but on the whole the percentage of CO_2 in the gas current increases as it ascends in the furnace. Furnace gases from the normal furnace will vary as indicated below:

	Per Cent
CO_2	9–14
CO	19–13
N	72–73

202. Products. From such a reducing fusion in the blast furnace the four following products are ordinarily obtained: matte, slag, speiss, and flue dust. With the exception of the slag these are all intermediate products and must be treated by other processes in order to obtain the copper and valuable by-products.

The matte will contain from 15 to 50 per cent of Cu besides varying percentages of Au, Ag, As, Sb, Bi, and other impurities. The matte is usually collected in the forehearth until a sufficient quantity has accumulated to make it worth while to send it on to the converting department to be reduced to blister copper or cast into pigs for sale.

The slag will contain, with modern processes and apparatus, from 0.25 to 0.55 per cent of Cu. A part of this is mechanically entrained, and a part is dissolved in the slag. The slag is usually a waste product, but at some smelters it is saved in hope that processes may be developed whereby this small amount of copper can be extracted at a profit. Some of the hydrometallurgical processes are being successfully applied to ores almost as low grade as these slags. In small plants the slag is allowed to run into slag pots, and these are taken out from time to time to be emptied on the slag dump. In larger plants the stream of slag is allowed to fall into a launder in which a current of water is running. This causes it to break up into small granules or drops, which are carried away by the running water to a waste dump.

A speiss consists of arsenides and antimonides of the base metals, chiefly Cu and Fe. It will not be formed unless the original ore contains considerable As or Sb which have been imperfectly eliminated in the roasting. Sometimes a speiss is purposely made in treating copper ores containing Ni in order to collect the Ni in the speiss and the Cu in the matte. The treatment of a speiss when so produced consists of a series of oxidizing roasts followed by reducing fusions.

Flue dust consists of both changed and unchanged particles of ore, flux, and fuel carried off by the gas current as it emerges from the top of the furnace. This current has a considerable velocity and will transport particles as coarse as fine sand. This flue dust is settled out in large chambers or is precipitated by Cottrell apparatus, for it usually contains enough Cu, Ag, Au, and As to make its recovery well worth while.

203. Recovery. The recovery of the metal in the smelting of sulphide copper ores is high, provided they are not contaminated with compounds of Zn and Pb, which cause irregular operation of the blast furnaces. The only losses are through the slag and the flue dust, and in modern plants these can be kept very low. The recovery of copper should be in the neighborhood of 97 per cent, that of silver 98 per cent, and that of gold 100 per cent.

204. Operation. Furnace operation may be divided into blowing-in, routine operation, and blowing-out.

In blowing-in a furnace a light wood fire is kept burning in the crucible of the furnace for twenty-four hours. It is then

cleaned out, filled again with light wood and cordwood up to the tuyère level, and ignited from end to end. Air may or may not be blown in through alternate tuyères (the others being plugged); this depends upon the condition of the wood. Often the natural draft through the tuyères is sufficient to keep a fire burning briskly. When a firm bed of coals has been obtained, coke is charged in to the amount of about 45 pounds per square foot of hearth area, a light blast is turned on, and the plugged tuyères are uncovered. When this coke has become thoroughly ignited and red on top, the furnace receives its first charge. The first five or six charges differ from the routine charge in that they are less siliceous and contain as high as 50 per cent of coke. In about an hour sufficient slag has collected in the crucible to close the trapped spout. Matte and slag then overflow into the preheated settler, the blast is turned on full, and the furnace is ready for routine operation. It is advisable to proportion the initial charges so as to produce a matte of from 30 to 35 per cent Cu, for this runs hot and serves to heat up the crucible and forehearth quickly. At some smelters the first charges contain a large proportion of barren slag which helps to heat up the furnace and fill the crucible and forehearth with molten material.

In the routine operation of the furnace weighed charges of ore, flux, and fuel are brought to the furnace in charge cars holding from $\frac{1}{2}$ ton to 2 tons. Furnaces are usually fed from both sides, and considerable care must be taken to distribute the charge evenly over the furnace; otherwise the blast and heat will be concentrated in one part of the furnace, while the other parts may be dead and inactive. A blast furnace is not suitable for the treatment of fine ore, and if such material is used it must be well mixed with the charge and evenly distributed through it. In small furnaces the slag and the matte accumulate in the crucible, and the separation of the two takes place there, but care must be taken that the slag does not rise too high and flow into the tuyères. In the large furnaces there is a continuous overflow of matte and slag into the forehearth, where the separation takes place. Slag overflows continuously from the forehearth, where the matte is allowed to collect and is removed from time to time as it is required by the converting department.

When the furnace is shut down, slag charges are substituted for ore charges until most of the ore has been smelted. The charging is then stopped, and smelting is continued until the slag has been lowered to a point just above the tuyères. The tuyère valves are then closed, the crucible tapped clear of both matte and slag, the breast jacket removed, and the contents of the furnace raked out. If much ore is left undecomposed, the material is set aside and added to the routine charges when the furnace starts up again. It is obvious that the secret of success in the operation of a blast furnace is continuous operation. Short delays and shutdowns are expensive and interfere seriously with the efficient operation of the furnace.

205. Adding fuel through the tuyères. It would appear logical to blow in fuel and flux with the air of the blast instead of laboriously charging these from above. Many attempts have been made to utilize powdered coal introduced into the tuyères, but they have not been successful.

206. Blast. In copper smelting the blast is hardly ever preheated. The blast pressure will depend upon the width of the furnace, the diameter and the number of the tuyères, the percentage of Fe, and the physical character of the charge. In the United States blast pressures vary from 25 to 60 ounces per square inch, with 40 as perhaps the most common. In smelting at high altitudes, owing to the decreased percentage of O in the air, the blast pressure may be increased, but it is better practice to increase the number of tuyères in order to keep up the capacity. A high blast pressure tends to make an excessive amount of flue dust.

PYRITIC SMELTING

207. General. In pyritic smelting an attempt is made to utilize the heat of combustion of the sulphur, and the heat of formation of ferrous silicate, to promote the reactions of matting and slagging and to keep the contents of the crucible molten. The leading exothermic reactions are

$$FeS + 3\,O = FeO + SO_2,$$
$$FeO + SiO_2 = FeSiO_3 \text{ (slag)}.$$

For such smelting a high-sulphur ore is necessary, and while theoretically there is sufficient heat generated to keep the fur-

nace in proper condition, actually it is usually found best to add from 1 to 3 per cent of coke to the charge. Such pyritic furnaces, however, have worked for days at a time without the addition of any coke whatever. Usually 3 per cent of coke is taken as the limit; above that figure we call it partial pyritic smelting. The three essentials for true pyritic smelting are a pure pyrite ore, free from combined SiO_2, and ample air. The combined silica usually present is not only not available for the slagging of the iron and other bases present in the ore, but its liquefaction absorbs heat that is needed to keep the furnace hot.

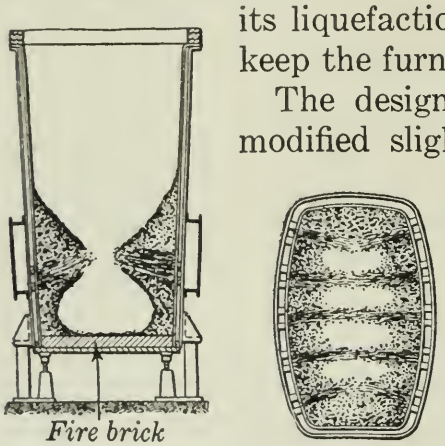


FIG. 76. Pyritic smelting

The design of the pyritic furnace must be modified slightly from the ordinary type, for air has to be supplied in much larger quantities. For example, the O required in a reducing fusion with 13 per cent of coke is much less than that required for the oxidation of the Fe and S in pyritic smelting.

Fig. 76 shows a vertical section of a furnace under blast in pyritic smelting. It has a very different appearance from one being operated on an ordinary reducing fusion. In the latter the sides of the furnace are slightly coated with half-fused or partly decomposed material, but in the main the active part of the furnace follows the configuration of the sides of the furnace. In pyritic smelting the charge forms a bosh extending along the side walls of the furnace and out into the furnace. The thickness of this bosh depends upon the physical and chemical conditions prevailing in the furnace. The tuyères are almost bridged with a porous, friable material composed mainly of half-fused ore and flux. The blast in passing through this porous mass is warmed and exerts a powerful oxidizing effect upon the drops of fused sulphides trickling down from above.

208. Chemistry of blast-furnace smelting. Let us consider first the descending ore charge. In the first 7 or 8 feet of the furnace shaft, where the temperature varies from 250 to 700° C., the charge gives up its hygroscopic water, and pyrite gives off one molecule of S: $FeS_2 + \text{heat} = FeS + S$.

As the charge sinks lower in the furnace it begins to give off CO_2 from the dissociation of the limestone of the charge. At about 900° C. the FeS is fused and trickles down over the white-hot pieces of SiO_2 and CaO. It meets the oxygen of the blast, is oxidized to FeO, and unites immediately with SiO_2 to form a fusible silicate, thus adding heat to the charge. The silicate then absorbs CaO and the other bases of the ore to form a slag.

All the FeS is not burned. Conditions are so maintained that there is enough left to form a matte with the Cu_2S. This melts and trickles down through the charge, absorbing Au and Ag from the ore.

The blast of air enters the furnace through the porous bosh and bridge, is warmed, and then strikes, a short distance above the tuyères, the molten FeS trickling downward. A large part of it is oxidized to SO_2 and FeO. The latter unites with SiO_2 to form a slag. A short distance above the tuyères the gas mixture will be N and SO_2, and the temperature of this about 1200° C. As this gas ascends through the furnace it warms the charge. Four or five feet below the top the charge will begin to give off S at a temperature of 700° C.:

$$FeS_2 + \text{heat} = FeS + S.$$

The sulphur vapor thus produced will rise to the top of the furnace, where it will burn with a short blue flame. The following analysis of gases from the top of the furnace indicates that the O of the blast is almost wholly consumed in the oxidation of the FeS. Compare this analysis with that from a reducing fusion on page 152.

	Per Cent
SO_2	6–10
CO_2	2–5
CO	0–0.2
O	0–1.5

209. Operation. Great care is necessary in the operation of a pyritic furnace. The charge must be of uniform composition and sufficiently high in S to keep the furnace hot. Light wall accretions which would cause little difficulty in a reducing fusion are the source of considerable trouble. A change in the moisture of the air (with a corresponding change in the O content) or in the character of the slag and the charge — in fact, any slight irregularity — is sufficient to interfere with the process. The

elimination of As, Sb, Bi, and Pb is much greater than in a reducing fusion. Once a furnace gets out of order it has been found better to blow it out and start afresh than to try to save it by the addition of larger percentages of coke.

210. Two-stage smelting. Ores containing as little as 2 per cent Cu are sometimes smelted in a blast furnace. Sometimes they are massive, pyritic ores, and at other times more siliceous ores with enough gold and silver to pay for the operation. In either case a concentration of 10 : 1 is as much as can ordinarily be obtained, producing a 20 per cent matte. Such a matte would be too low grade to be economically converted. At Ducktown, Tennessee, for example, the ore is smelted to a 10 per cent matte, and this is then resmelted in a pyritic furnace to produce a 45 per cent matte, which is admirably adapted to converting. The slag from the second fusion is too high in copper to be thrown away; so it is returned to the first furnace for re-treatment. Another method, to be taken up in detail under reverberatory smelting, consists in roasting the matte to remove the S, and then smelting in a reverberatory furnace. Where it is possible such two-stage smelting is to be avoided, for it is naturally more expensive and the loss of copper is higher.

PARTIAL PYRITIC SMELTING

211. Ore. As the name implies, this process is carried out on ores which do not contain enough S for pyritic smelting and yet do not require roasting and the use of as much as 16 per cent of coke. In partial pyritic smelting the coke constitutes 8 per cent and upward, by weight, of the charge.

REVERBERATORY SMELTING

212. General. In the reverberatory furnace the carbonaceous fuel has but little reducing action upon the charge. The furnace is primarily a heat-producing one, and the reduction and concentration of the copper is brought about through preliminary roasting and reactions between Cu_2S and Cu_2O. For successful reverberatory work we must have self-fluxing ores or ores which require only a small amount of flux, cheap silica brick (ordinarily the slag is an acid one), and, since the process con-

sumes large amounts of coal or oil, cheap fuel. The charge must be free from lump ore and requires a careful preliminary roast. It is admirably adapted to the treatment of concentrates and fine ores. These, in the blast furnace, produce excessive amounts of flue dust with a corresponding high loss of copper and precious metals.

THE REVERBERATORY FURNACE

213. General. The reverberatory furnace, shown in Figs. 77 and 78, is similar in principle to the furnace employed in roasting. The temperatures attained are much higher, so that the lining must be more refractory and there must be a smaller ratio of hearth area to grate area. The hearth, instead of being flat or arranged in steps, must be cup-shaped to facilitate the collection of the matte and slag as well as its easy removal from the furnace. The furnace illustrated has a hearth 80 feet long and 20 feet wide.

214. Hearth. The foundation of the furnace may be either concrete or poured slag. On top of this is placed the hearth proper. This must be of very refractory material to resist the high temperature and corrosive action of the slag and matte. It must also have considerable mechanical strength at this high temperature, in order to resist the pressure of the heavy bath of matte and slag which accumulates on the hearth. Sintered silica is the most popular hearth material, for it is cheap and easily applied, and resists well the acid slags used in reverberatory smelting. This silica must contain at least 95 per cent of SiO_2. The working bottom is prepared by shoveling in sufficient material (crushed to pass $\frac{1}{4}$ inch) to cover the foundation to a depth of 24 inches. The bottom and sides are shaped by men with shovels, to give the proper drainage and banks. The bottom should be about 20 inches below the skimming hole. When the bottom has been shaped and patted firmly into place, a light fire is started and the bottom thoroughly dried out for several days. The temperature is then raised so that at the expiration of about forty-eight hours the bottom is glazed over with fused material (temperature, from 1450° to 1650° C.). The heat is then turned off, and the furnace is tightly sealed and allowed to cool very slowly, so that the bottom may be

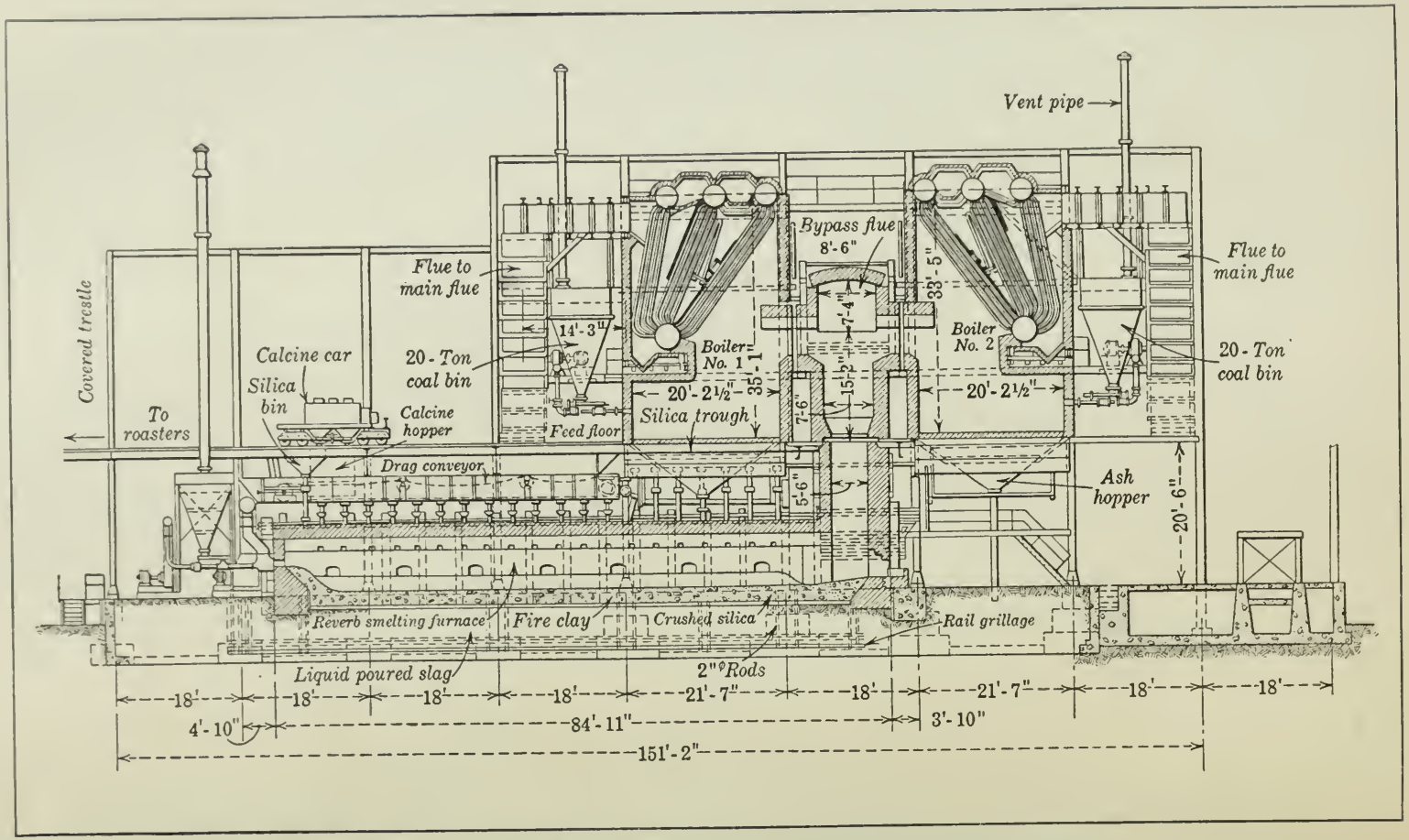


FIG. 77. A longitudinal section of a reverberatory smelting plant

annealed and so be less liable to breakage, or spalling, when smelting is started. This takes about forty-eight hours. At the Canada Copper Company, operating on a copper-nickel ore, a basic hearth of magnesite brick has been tried out with a high degree of success. Chrome brick is often used at the slag line to keep down the corrosion due to the formation of FeO.

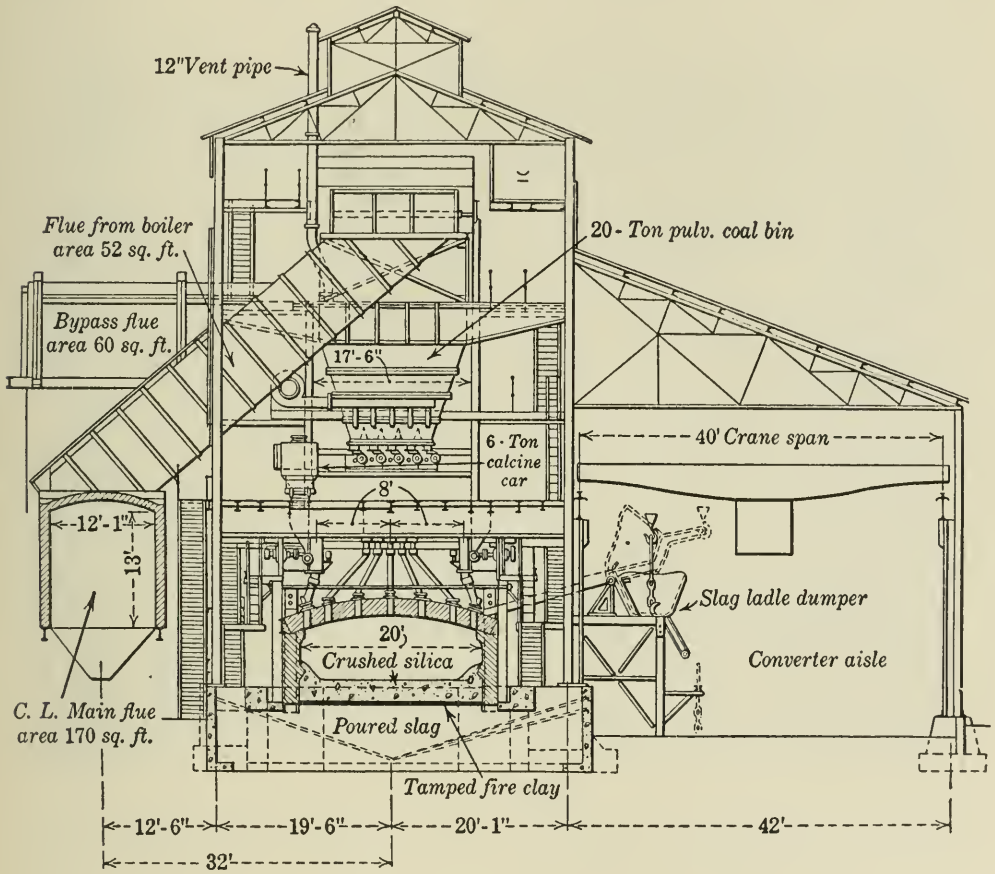


FIG. 78. A cross section of a reverberatory smelting plant

On both sides of the furnace, at frequent intervals, are small openings with sliding doors that fit tightly. Through these the operators may watch the changes in the contents of the furnace and rabble, or stir the charge if it is found necessary. Temporary repairs to the bottom and the side walls can also be effected through these doors.

215. Roof. The general shape of the roof must be such as to reflect the flame from the combustion of the coal or oil down onto the charge on the hearth. The efficiency of the furnace will depend largely upon the contour of this roof. Silica brick

is almost universally used for its construction. The thickness of this will vary from 12 to 18 inches.

216. Firing. Most modern plants use either pulverized coal or fuel oil, the choice depending upon local conditions. The amount of coal consumed in a large furnace will vary from 275 to 400 pounds per ton of charge; the amount of fuel oil, from 0.6 to 1.5 barrels per ton of charge. Fig. 79 shows the

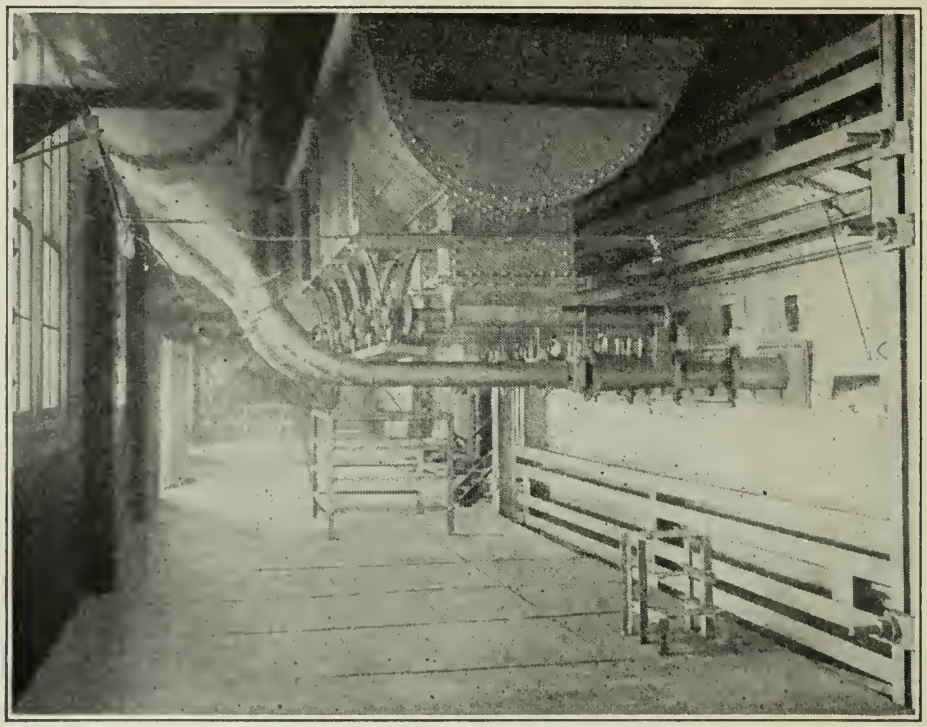


FIG. 79. The firing end of reverberatory furnace (pulverized coal)
Courtesy of the Anaconda Copper Mining Company

firing end of one of the large reverberatory furnaces at the Anaconda Copper Mining Company using pulverized coal. There is a considerable loss of heat in the waste gases from these furnaces, since they leave the furnace at a temperature of 1200° C. At most modern plants waste-heat boilers are used, as indicated in Fig. 77. The power thus generated can be used to provide electricity for general use about the plant. As much as 35 per cent of the heat can thus be saved.

217. Charging methods. The old method of charging was to drop large charges of ore and flux onto the hearth through hoppers located along the center line of the furnace, near the

fire-bridge end. These large charges, even with constant rabbling by the operators, took some time to melt down, and interfered with the best working of the furnace. They were dropped about every three hours, but even large charges of from 5 to 15 tons at these long intervals appreciably lowered the temperature of the furnace.

The usual method today is to employ the continuous method of side charging. The hot calcined ore is introduced into the

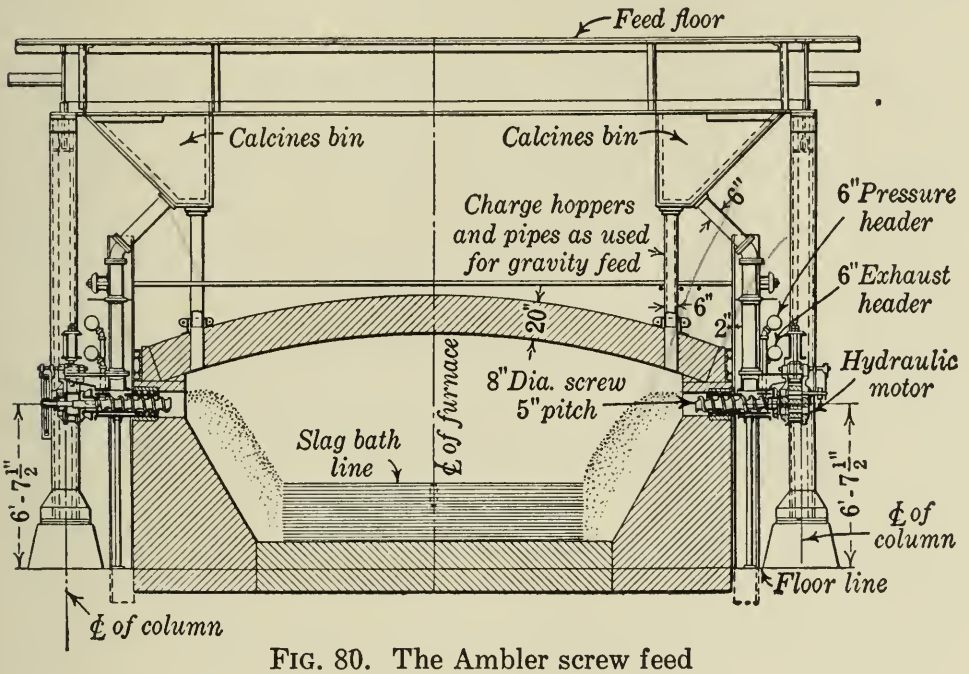


FIG. 80. The Ambler screw feed

furnace through holes along the sides. These are distributed along both sides of the first 25 to 30 feet of the firing end. There are several hoppers to serve these charging holes. At several plants, introducing the charge by means of plungers has been tried with some degree of success. At the Copper Queen Smelter the Ambler screw feed, illustrated in Fig. 80, has succeeded in reducing the dust loss very materially. Side charging protects the side walls of the furnace from the mechanical wear of the charge, as well as from the corrosive action of the slag and matte, and in general prolongs the life of the roof by cutting down spalling and cracking. Ore used to be charged cold, but today considerable saving is effected by bringing the hot calcine direct from the roasters and charging it into the furnace before it has had a chance to cool.

A modern reverberatory-furnace installation with waste-heat boilers is shown in Figs. 77 and 78. The hearth of the furnace measures 80 feet long by 20 feet wide. The walls and roof are of silica brick, — the former 24 inches, the latter 20 inches in thickness. The bottom is made up of 7 feet of poured slag, 4 inches of fire clay, and 27 inches of silica. The gases from the furnace go to two Stirling waste-heat boilers. These gases may be by-passed for boiler repairs, or the boilers may be operated independently of the furnace when it has to be shut down for repairs.

The roasted material is dropped into one of three fettling hoppers, one serving the five fettling pipes at the bridge wall, the others serving the fettling conveyors along the sides. Most of the material is smelted in the first 40 feet of the furnace. On each side of the remaining 40 feet are seven fettling pipes through which siliceous ore is fed to the furnace. Slag overflows continuously from the furnace. Four matte tap holes (lined with chrome brick) are provided along the side. As a rule only two of these are ever used, the others serving as spares in case of a choke-up. The method of charging converter slag is also indicated.

218. Chemistry of reverberatory smelting. The reverberatory can be best considered as a huge melting furnace, for there is very little reduction by the carbonaceous fuel. This is practically all consumed in producing heat. As indicated in Fig. 80, the charge, fed into the furnace from the side, forms a V-shaped pile along the side. The molten material flows down this slope and collects in the bath of matte and slag in the center of the hearth. Partially fused material also slides down this slope and floats about on the slag until absorbed or decomposed. Charging is confined to the first 20 or 30 feet of the fire-bridge end, and with the high temperatures used today all this material is completely fused and separated before it reaches the flue end to be tapped off. The reactions which go on are complicated, since the charge consists of a complex mixture of sulphates, oxides, sulphides, arsenides, etc. in varying proportions. The reduction of Cu_2O begins at 500° C. and is complete at 1000° C.:

$$Cu_2S + 2\,CuO = 4\,Cu + SO_2,$$
$$Cu_2S + 2\,Cu_2O = 6\,Cu + SO_2,$$
$$Cu_2S + 3\,CuO = 3\,Cu + Cu_2O + SO_2.$$

The copper thus set free is immediately sulphurized and unites with pyrite to form a matte:

$$2\,Cu + FeS = Cu_2S + Fe.$$

Any unreduced copper oxide is similarly sulphurized:

$$Cu_2O + FeS = Cu_2S + FeO,$$
$$6\,CuO + 4\,FeS = 3\,Cu_2S + 4\,FeO + SO_2.$$

In case any copper silicate is present in the ore, or has been formed, owing to improper roasting, it will be sulphurized and matted:

$$Cu_2SiO_3 + FeS = Cu_2S + FeSiO_3.$$

Iron oxide is reduced as follows:

$$3\,Fe_2O_3 + FeS = 7\,FeO + SO_2,$$
$$Fe_2O_3 + CO = 2\,FeO + CO_2.$$

This FeO unites with SiO_2 in the ore to form a slag:

$$FeO + SiO_2 = FeSiO_3.$$

Zn, Pb, As, and Sb are partly volatilized, partly matted, partly scorified, while the precious metals are dissolved in the matte.

219. Products. These are similar to those produced in the blast furnace; namely, matte, slag, speiss, and flue dust.

Mattes vary in copper content from 15 to 50 per cent. This percentage is governed entirely by the preliminary roasting and the operation of the furnace. A much higher ratio of concentration is possible than in the blast furnace.

The slags formerly produced in the reverberatory furnace (owing to the low temperature attained) used to run high in copper, owing to unsettled matte in the slag. Today, with pulverized coal or oil fuel, temperatures up to 1500° C. are possible. With such high temperatures the slag is more fluid and runs easily from the furnace (formerly it had to be raked out). Reverberatory slags are, as a rule, slightly higher in copper than blast-furnace slags. This may be due to the fact that the matte has not so good an opportunity to settle out as it has in the blast-furnace forehearth, but it seems more likely that it is due to fine ore from the charging operation. This falls upon the slag, is caught, and flows out with the slag before it can be decomposed.

The gases from the reverberatory leave at a temperature of about 1200° C.; so in most modern plants it is usual to con-

serve a part of this waste heat by passing the gases under boilers where the temperature is lowered to about 400° C. This operates under some disadvantages: the flue dust settles out and clogs the passes of the boilers, and the sulphurous gases corrode the boiler tubes rapidly and necessitate frequent and expensive repairs; but, on the whole, such installations effect very considerable savings in operation. From the boilers the flue gases go through a dust-precipitating plant, where the flue dust is recovered. Such apparatus will be treated in detail under the chapter on lead.

220. Operation. A furnace, once in operation, is charged every one and one-half hours with about 15 tons of calcined ore and flux. This is dropped into the furnace through hoppers located at the fire-bridge end of the furnace. If charged through the side the operation is continuous. In either case, in the intense heat of the furnace, the charge is rapidly melted down and joins the pool of slag and matte on the hearth of the furnace. If the furnace is of the intermittent type, from 40 to 60 tons of slag is removed from the furnace every three or four hours. Otherwise the slag overflows continuously. The level of the matte is kept fairly constant, being tapped from time to time as needed for converting.

The slag, especially in top-charged furnaces, tends to corrode the sides of the furnace. When these require repair, the furnace is drained completely of slag and matte, the side doors are opened, and refractory material can be thrown across to repair holes eaten in the walls by the slag. Such repairs are usually effected without losing all the initial heat of the furnace. At longer intervals (every four to six months) the furnace must be completely shut down for repairs to the roof, fire bridge, and walls.

Only a relatively small proportion of the heat from the combustion of the fuel is actually used in the smelting operation, as shown by the following approximate heat balance:

	Per Cent
Heat in matte	3.0
Heat in slag	16.4
Radiation	11.9
Heat in waste gases	33.8
Heat used in generation of steam	34.0
Heat in ashes	0.9
Total	100.0

The temperature in a modern reverberatory varies from 1550° C. at the fire bridge to 1200° C. at the flue end. The gases leave the waste-heat boilers at a temperature of about 350° C.

221. Blast-furnace versus reverberatory smelting. Blast furnaces do not operate well on fine ores. Not only is there a large loss of valuable metals through the formation of an excessive amount of flue dust, but this fine ore is sintered and tends to clog the furnace. A large and increasing proportion of our metal is coming from concentrates which vary in size from $\frac{1}{4}$ inch down to the finest dust. Such material is best treated in a reverberatory furnace, for the relatively quiet fusion there cuts down the loss through flue dust. On the other hand, lump ore cannot be economically smelted in a reverberatory furnace. It is difficult to charge, it cannot be successfully roasted in furnaces of the Wedge type, and the dropping of such heavy pieces on the hot hearth tends to damage it.

A few years ago, after the large reverberatories at Anaconda were placed in operation, the prediction was freely made that they would supplant the blast furnaces. While reverberatories undoubtedly have many advantages, they can never take the place of the blast furnace in treating lump ore. As a matter of fact, as regards cost it is about a stand-off between nodulizing or sintering and reducing in the blast furnace and roasting and smelting in the reverberatory. Experiments looking toward the injection of pulverized fuel with the blast are now being conducted. If these should ever be successful it will give the blast furnace a very decided advantage.

222. Costs. These will vary according to the character of the ore and according to local conditions. Blast-furnace costs will vary from $1.75 to $3.00 per ton of charge.

Reverberatory costs will vary from $2.00 to $3.50 per ton of charge and will be distributed approximately as follows:

	Per Cent
Fuel	50
Labor	10
Repairs	13
Slag and matte handling	7
Ore handling	20
Total	100

SMELTING NATIVE COPPER ORE

223. General. In the Lake Superior copper district the ore containing native copper is passed through various ore-dressing processes, and the concentrate, or "mineral," smelted in a reverberatory furnace to pure copper. This material is divided into mass copper, barrel work, headings, and grades, so called, according to the size and the copper content. The mass copper comes directly from the mines in pieces weighing from a few pounds up to several tons. The grades of concentrates vary from the finest slime up to those 1 inch in diameter and having a copper content of from 30 to 70 per cent. The average of the four classes is 60 per cent Cu.

224. Process. The smelting of this material is carried out in a reverberatory furnace. The ore is mixed with limestone as a flux and given an oxidizing fusion. The resulting slag is skimmed off, the copper refined (sometimes in the same furnace), as described later under "Fire Refining of Copper," and cast into a suitable form for marketing. Formerly the slags were so high in Cu that they had to be re-treated, but today, by mixing the charge with coal to reduce the copper, and with iron or silica to form a slag, it has been found possible to produce a slag with a copper content as low as 0.8 per cent. At plants where the slags run higher than this such slags are re-treated in a blast furnace.

CONVERTING

225. General. In the converting of copper mattes, air in minute bubbles is forced through the molten material contained in a vessel lined with a suitable refractory material. The sulphur is oxidized and escapes through the mouth of the converter as SO_2. The FeS is oxidized to FeO and unites with the SiO_2 to form a slag, while the Cu_2O and Cu_2S react to form metallic copper and SO_2. The oxidation of the Fe and S and the heat of formation of the ferrous silicate furnishes sufficient heat to promote the reactions of converting and to keep the contents of the converter molten. The lining of the converter may be either acid or basic, the latter being almost universally used at the present time. Converters may be further classified as upright or horizontal, according to the shape of the vessel.

THE COPPER CONVERTER

226. Upright type. This is sometimes referred to as the Great Falls type, since it was developed at the Great Falls plant of Anaconda Copper Mining Company. A small converter is shown in Fig. 81. It consists of a cylindrical shell of boiler iron *a* lined with a suitable refractory *b*. While the illustration shows a brick lining, the converter is often lined with ganister. This (mixed with a binder) is rammed into place around a mandrel. The shape must be such that when the converter is tipped on its side, exposing the tuyères, there will still be ample space in the belly of the vessel to hold the charge of matte, slag, and metal. It is supported by trunnions *d*, of which one is hollow and serves to conduct the air to the tuyères *g* through the wind box *e* which encircles the converter. The shell is made up of four parts: the hood, middle part, lower part, and bottom. The peculiar shape of the lining is due to the fact that the lining corrodes unevenly, the greatest corrosion being near the tuyères and at the slag line. The converter top, as indicated, comes apart just above the trunnion, so that the lower part may be taken to one side for relining and another quickly bolted into place. Trunnion *d* is connected through a proper stuffing box to the air main which supplies air at a pressure of from 12 to 20 pounds per square inch. Each tuyère has a flap valve to permit punching of the tuyères when they become clogged with pasty matte or metal. Such a converter will take an initial charge of about 5 tons of matte, and by successive blowing and charging will deliver about 8 tons of blister copper.

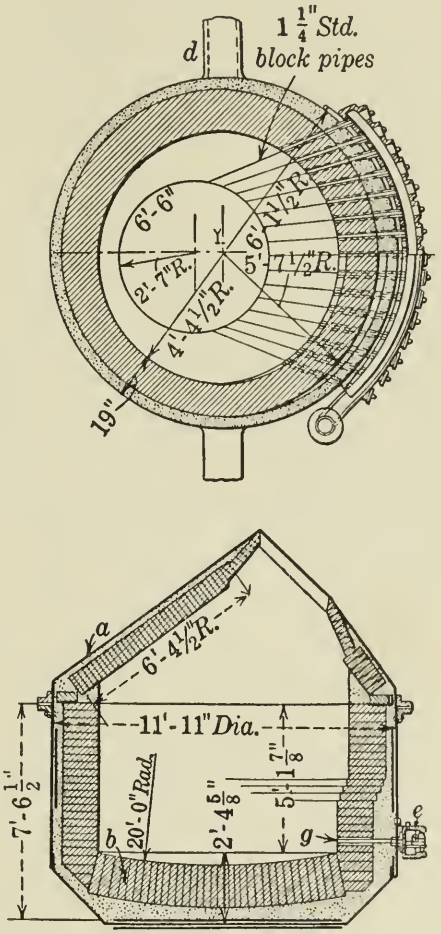


FIG. 81. An upright converter

Upright converters are usually operated with an acid lining. If a basic lining is employed for any reason, the siliceous ore for fluxing must be charged by means of a "boat" through the open mouth of the converter. These upright converters are now made very much larger than indicated in the sketch. The 12-foot (diameter) converter at Great Falls takes an initial charge of 16 tons of matte. After a blowing campaign of from 5 to 7 ladles it will deliver about 15 tons of blister copper.

227. Horizontal type. This type of converter is shown in Fig. 82. It consists of a horizontal barrel, or shell, of boiler

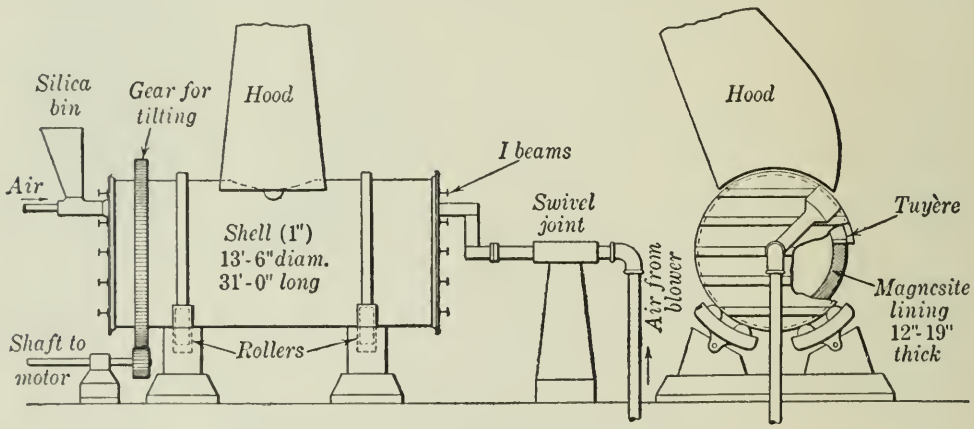


FIG. 82. Horizontal converter

iron, lined with a refractory material, usually of a basic character. At each end of the steel shell are rings which ride upon four rollers and carry the weight of the converter. At one end of the converter is a large gear and pinion by means of which the converter can be tilted for inspection and pouring. There is a rectangular wind box along the front, supplying air to the tuyère pipes. This air is brought to the converter through the large main. It is provided with a suitable stuffing box, so that the converter can be tilted while still on air.

The horizontal type of converter is made in very large sizes. One is 13 feet in diameter and 30 feet long, and has 41 tuyères, each $1\frac{1}{4}$ inches in diameter, placed at $6\frac{1}{2}$-inch intervals. Such a converter, working on a 40 per cent matte, will produce from 110 to 125 tons of blister copper. The horizontal converters are provided with a charging device (silica gun) in the end of the converter barrel, so that siliceous flux can be added without tipping up the converter in order to insert the boat or remove the hood.

228. Hoods. Both the upright and the horizontal converters are provided with some sort of hood fitting tightly over the mouth. It serves two purposes: first, to keep fume and dust out of the converter aisle and provide better working conditions for the operators; second, to save this flue dust and fume for treatment. The flue dust contains copper and valuable by-products, while the fume is used in the manufacture of sulphuric acid or liquid SO_2.

CONVERTER LININGS

229. Acid linings. The acid lining must contain a large percentage of free SiO_2 and be mechanically strong. The former is essential in order to slag the FeO as it is formed, and thus keep the converter hot. Pure pulverized SiO_2 has no mechanical strength; so it is usually necessary to add a small amount of clayey material to give it the requisite plasticity for molding it into place, and at the same time to supply a small amount of base to sinter, or flux, it. At first operators were careful to use a very pure flint or quartzite, but today siliceous ores containing precious metals are almost universally employed. Such ores could not be marketed for their precious-metal content alone, but when employed as an acid lining they give up these precious metals to the matte. While theoretically these impure siliceous ores are not so good as pure flint or quartzite, practically they are better, for this low-grade ore is thus smelted for nothing.

An acid lining is rapidly corroded by the charge and will last only from 6 to 9 heats, or about twenty-four hours. The converter shell must then be removed for relining; otherwise the outside shell would be attacked by the matte and slag, and ruined. This relining is a slow operation, and it is good practice to have several spare converter shells ready, so that as one is corroded it can be removed and another (already dried, annealed, and warmed) slipped into its place on the converter stand. These shells involve the investment of considerable capital and necessitate loss of time; these disadvantages constitute the chief reasons for using the basic lining, which has a much longer life.

In converting low-grade mattes (those very rich in iron) the lining is rapidly corroded and may last only two or three blows. Another objection is the spalling or flaking of siliceous material

when subjected to the sudden changes in temperature necessary in the converting operation.

230. Basic linings. This frequent relining of acid converters led to experiments with neutral materials or those less easily attacked than SiO_2. A great many materials were tried, but the most successful, and the one almost universally used today, is magnesite brick. The SiO_2 for fluxing the FeO is dumped into the converter in the form of pulverized quartzite or siliceous ore. The converter is lined with magnesite brick varying in thickness from 24 inches at the tuyères, where the wear is greatest, to 9 inches in the upper part of the shell. It has been found that by blowing matte at a low temperature or in the presence of little or no SiO_2 a considerable quantity of Fe_3O_4 separates out from the charge and attaches itself to the lining. It penetrates the cracks between the bricks and forms a protective coating over the magnesite. If it were not for spalling and flaking, due to the sudden changes in temperature during converting, a basic lining would last almost indefinitely, for it is not attacked chemically by the charge. As it is, these basic linings last for several months, converting from 2000 to 2500 tons of Cu per ton of lining as against 10 tons with acid lining.

231. Lining converters. The acid lining is easily applied by tamping the mixture of clay and siliceous material about a mandrel inserted in the shell of the converter. Pipes inserted in the bottom form the mouths of the tuyère openings. This lining must be carefully dried, annealed, and fired before the initial charge of matte is placed in it.

The lining of a basic converter is a longer and far more expensive process. The lining is in the form of brick (some of these have to be of a special shape) and must be carefully laid and cemented into place. This new lining is dried and warmed with a wood fire from thirty-six to forty-eight hours. It is then brought to a red heat, charged with two ladles of 35 per cent matte, and blown (with small additions of fresh matte) until the cracks between the brick and the bricks themselves have been coated with magnetite. The matte is then poured off, this coating hardens, and the converter is ready for use. With good basic practice it is seldom necessary to reline a converter shell completely. The greatest wear is along the tuyère section, where entire new sections may have to be built in from time to time.

The rest of the converter lining can be patched and with proper care will last for a long time.

232. Basic versus acid linings. The main advantages of the basic lining are (1) decreased cost of lining, (2) the use of larger vessels with a corresponding saving of labor and power, (3) the ability to convert low-grade matte without excessive lining consumption, and (4) less handling of shells. The basic lining, however, has some disadvantages, the chief of which are (1) excessive punching of the tuyères, due to the formation of Fe_3O_4 about their mouths, (2) more time required for lining and repairing, and (3) excessive blowing-out of fine siliceous ore during the charging of the flux. On the whole the advantages of basic converting far outweigh the disadvantages, and it is almost universally used in the large plants today. For small plants the acid converter is undoubtedly the best.

233. Operation of basic converting. Since acid converting has been largely given up except in small plants, only the method of operating a large basic converter will be described in this text. To the hot converter is added 60 tons of molten matte with about 6 tons of dried quartz or siliceous ore for the purpose of fluxing the iron oxide. The blast is started and the converter turned up until the tuyères are covered. After about thirty minutes of blowing, considerable slag will have accumulated; so the converter is turned down, the blast shut off, and the slag poured. Another ladle of matte with a charge of siliceous ore is added, and that blown down. This sequence of blowing to white metal (Cu_2S), skimming the slag, and adding matte is continued until from 300 to 400 tons of matte has been converted into from 70 to 80 tons of blister copper. This campaign may have occupied from three to four days of almost continuous blowing. If a converter gets too hot, it may be cooled by charging scrap, cleanings from the converter aisle, ladle skulls, etc. or by tilting up the converter and allowing air to blow over the surface. If the converter gets too cold, it may be warmed by charging hot matte high in iron. The progress of the blow is usually judged by the appearance of the flame which issues from the mouth of the converter. The condition of the matte or metal, which depends upon the stage of the blow, may also be determined by tilting up the converter, inserting a rod of iron in the bath, and examining the drippings from this rod.

234. Chemistry of converting. When the blast of air from the tuyère mouth strikes the hot matte, the sulphur is oxidized and driven off. It is then that the magnetite which coats the lining is formed:

$$5\ FeS + \text{heat} = Fe_5S_4 + S,$$
$$Fe_5S_4 + 14\ O = 2\ FeO + Fe_3O_4 + 4\ SO_2.$$

The FeO thus formed unites with the SiO_2 of the flux (or the lining if the converter is an acid one) to form a slag and supplies a part of the heat to keep the bath molten:

$$FeO + SiO_2 = FeSiO_3.$$

The above reactions go on until all the iron has been oxidized and slagged and the converter is full of white metal (Cu_2S). At the beginning of the blow the flame is green; at this stage of the process it changes to a pale blue.

The blast of air, once the iron has been slagged, begins to oxidize the Cu_2S:

$$Cu_2S + 3\ O = Cu_2O + SO_2.$$

This Cu_2S reacts with the Cu_2O to form blister copper:

$$Cu_2S + 2\ Cu_2O = 6\ Cu + SO_2.$$

These reactions go on until the last of the sulphur has been eliminated. A large part of the As, Sb, and Bi are volatilized as oxides. The changes in the flame as these reactions go on will be characteristic, from the blue of the end of the slagging period to white, rose red, and finally a brick red, which indicates the end of the blow. The operator has to be very careful not to blow too far and run the risk of freezing the converter or of saturating the copper with Cu_2O.

235. Products. From the converting operation we obtain (1) blister copper, which usually contains Cu_2O, As, Sb, Au, Ag, etc. (most of these impurities detract from the valuable properties of the metal, so that it must be further refined and purified before it is suitable for use in industry), and (2) slag, containing from 1 to 7 per cent of Cu, which must be returned to the plant for re-treatment.

The losses in converting average approximately from 1 to 2 per cent of the Cu and from 2 to 3 per cent of the Ag. These losses are due largely to the formation of flue dust and the volatilization of the metal. The loss of gold is small.

TREATMENT OF FLUE DUST

236. General. The gases from the blast furnaces, reverberatories, roasters, converters, and refining furnaces escape with considerable velocity and at a high temperature, carrying with them fine particles of ore, flux, fuel, matte, metallic copper, and fume. The accompanying table, showing the analyses and quantities of flue dust produced in a large plant, indicates that its recovery and treatment is well worth while.

	Tons of Dust per Month	Cu	Ag (Ounces per Ton)	Au (Ounces per Ton)	Insoluble	FeO	S
		Per Cent			*Per Cent*	*Per Cent*	*Per Cent*
Blast furnace . .	2122	8.08	2.7	0.02	34.7	33.0	16.1
Roasters	457	10.2	3.6	0.02	37.6	27.1	21.3
Main dust chamber	1562	8.6	3.3	0.02	33.3	14.5	11.8

237. Flue-dust chambers. In treating the gases from a smelting plant the first object is to check their velocity and reduce their temperature. The arrangement of the flue system at the Anaconda Copper Company is typical of large plants. Feeder flues of brick (20 feet wide and 15 feet deep) bring the gases from the roaster, reverberatory, blast furnace, and converter plants to the main flue, which is built up the side of the hill behind the smelter. Hopper-bottomed bins are built into these flues to collect the flue dust that may settle, although most of it drops out in the main flue. The total rise from the lowest furnace to the bottom of the stack is 400 feet. The stack is 585 feet high, 75 feet in diameter at the base, and 65 feet at the top. It has a capacity of 4,000,000 cubic feet of gas per minute. The first half of the main flue is 60 feet wide and 20 feet high, with a V-shaped bottom which facilitates the collection and withdrawal of the flue dust. The last half of the main flue is built double, as indicated in Fig. 83, so that gases may be diverted while the hoppers are being cleaned out. This part of the main flue is 177 feet wide. The total flue dust recovered at the Anaconda plant is about 300 tons per twenty-four hours. About 40 per cent of this is deposited in the flue-dust chambers, and the rest in the Cottrell treater.

238. Cottrell treaters. The gases from a smelter, even when their velocity has been reduced to 3 or 4 feet per second and

cooled almost to atmospheric temperature, contain considerable fine dust and fume. This can be removed satisfactorily only by means of a Cottrell precipitator. The principle of this piece of apparatus is illustrated in Fig. 84. It consists of a number of vertical tubes (depending upon the character and volume of the gases to be treated) from 5 to 10 inches in diameter and about

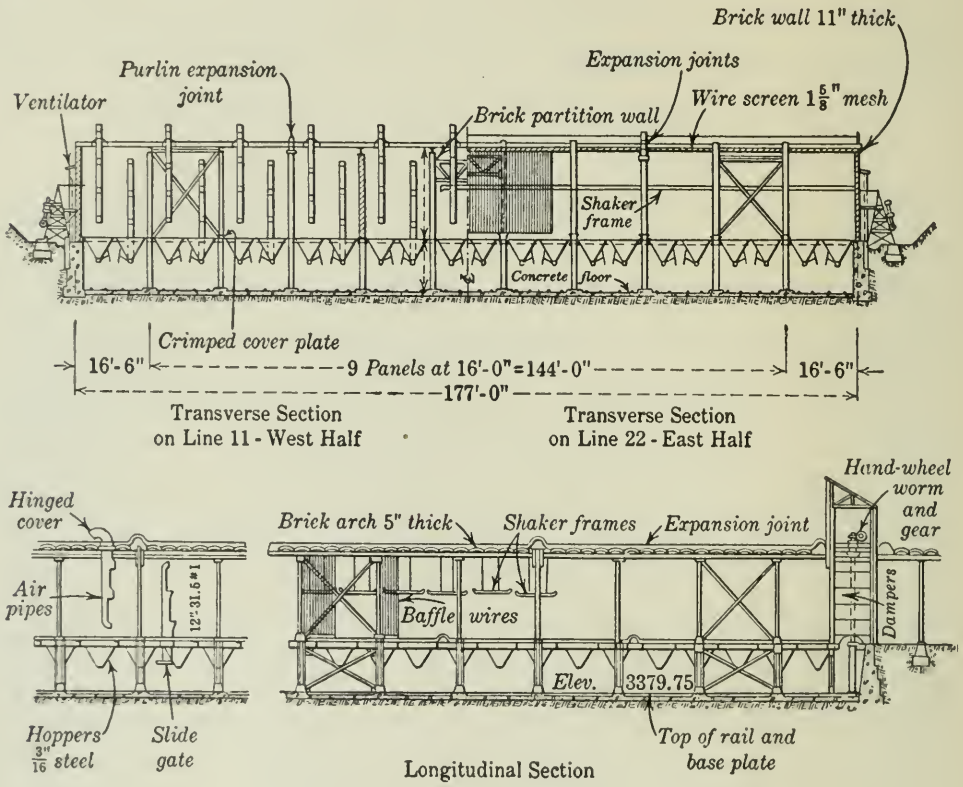


FIG. 83. Dust chambers

15 feet long. Suspended in the center of each tube and held in an axial position by a heavy weight, is a No. 10 insulated copper wire carrying a unidirectional current of from 25,000 to 60,000 volts. In operation the current passes from the wire to the inner surface of the tube, electrifying negatively the particles of dust and fume brought along by the gas entering the pipe at the bottom. These charged particles are then repelled to the inner surface of the tube and lodge there in the form of a coating. When this coating has accumulated to a sufficient thickness, the current is shut off for a moment and the tube is tapped mechanically, causing the flue dust to dislodge and fall into the bottom part of the chamber, where it may be drawn

off for treatment. At the International Smelter at Miami the Cottrell plant consists of 240 tubes, each 13 inches in diameter and 11 feet long. With 220 cubic feet of gas per second running through the tubes the velocity is 5.4 feet per second. The tubes are tapped every two hours.

239. Treatment of flue dust. Flue dust can be charged back into the blast furnace. As a matter of fact, at small plants this is the usual procedure. If this flue dust is dampened, some of

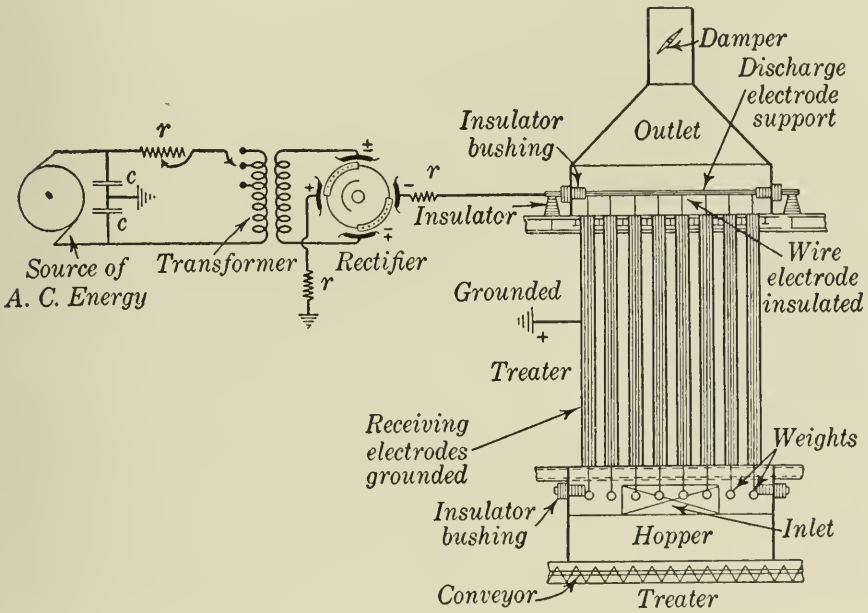


FIG. 84. A Cottrell treater

it will be carried down into the furnace and smelted, but most of it will go up the flue and eventually be lost in the atmosphere.

The most rational and effective way of disposing of this troublesome material is to briquette it. The raw flue dust is mixed with milk of lime as a binder in a horizontal pug mill similar to the one already described in connection with the manufacture of refractory brick. This mixture is then fed into a briquetting press, where it is made into briquettes of suitable form and weight. These briquettes may be used as they are discharged from the machine, but the usual plan is to air-dry them. In this condition they are not unlike ore, and when charged back into the blast furnace they make very little flue dust. Unless a plant is large enough to make a considerable tonnage of flue dust, however, such an elaborate arrangement is not worth while.

FIRE REFINING OF COPPER

240. General. Copper produced from the blast furnace or reverberatory and the converter contains considerable dissolved Cu_2O. If there is more than a certain limiting quantity (depending upon the other impurities present), the copper will be brittle and unfit for industrial uses. Such copper also contains As, Sb, Fe, Bi, etc. which were not volatilized or slagged in the converting process. All these impurities, although present

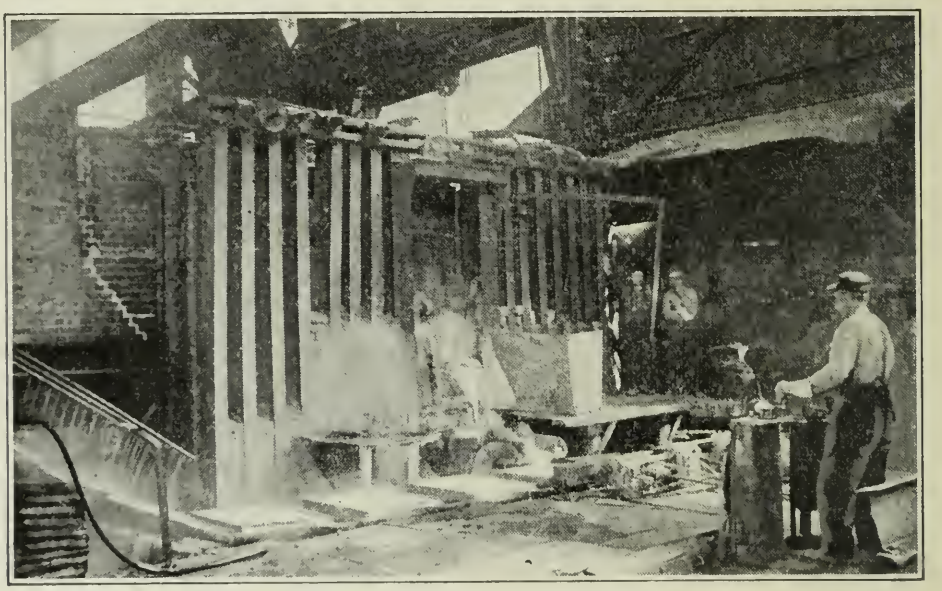


FIG. 85. A refining furnace

Courtesy of the Anaconda Copper Mining Company

in very small quantities, affect its electrical conductivity and detract from its mechanical properties. In case the ore contains precious metals these will be found in the resulting copper. The process of fire refining consists of an oxidizing fusion in a small reverberatory furnace. Some of the impurities are volatilized; others are oxidized and form with the copper oxide a slag which may be skimmed off. Finally, by a reducing fusion, the excess of Cu_2O is removed so that the copper contains about 0.4 per cent of Cu_2O and is then ready for casting.

241. Refining furnace. A reverberatory furnace for the fire refining of blister copper is shown in Figs. 85 and 86. Such furnaces have capacities of from 20 to 250 tons of copper. The bottom and the sides of the furnaces used to be constructed

of silica brick, and in the larger furnaces this refractory was cooled by means of air pipes embedded in the bottom and sides. Recently, following the converting practice, these furnaces have been built partly of magnesite brick and appear to stand the corrosive action of the charge very well. The roof has to withstand an intense heat; so it is always made of silica brick. The contact between the two consists of two or three courses of chrome brick to prevent slagging. Small furnaces are charged and cast by hand, but the larger furnaces employ some mechanical methods to cut down the cost of labor. Furnaces may be heated by either coal or fuel oil.

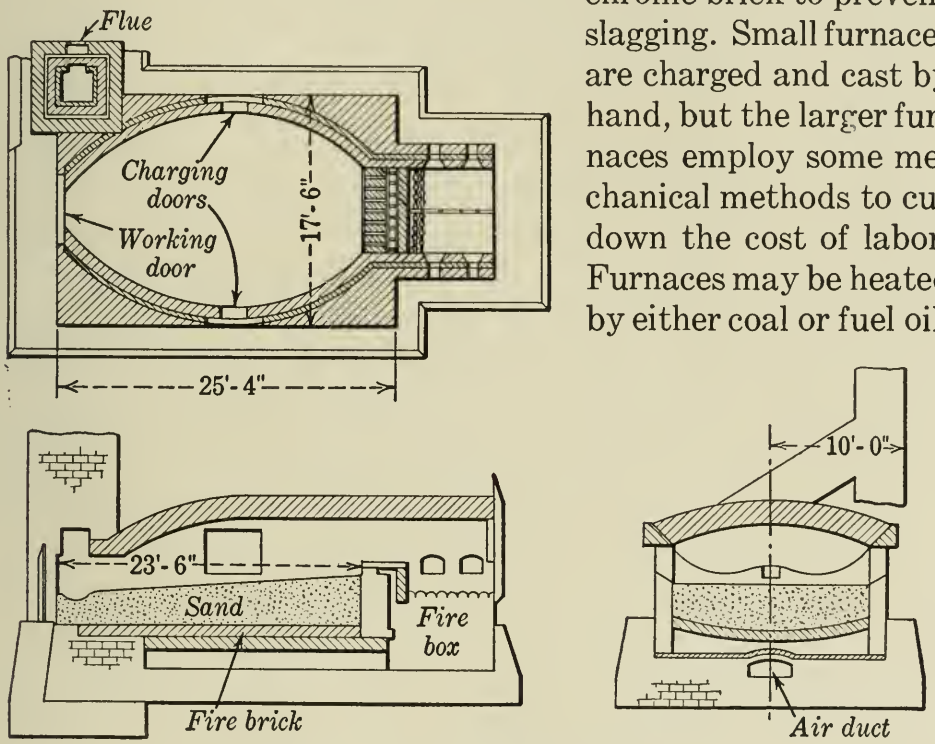


FIG. 86. A refining furnace

Since the temperature of the waste gases is high, the large plants use waste-heat boilers to conserve a part of this heat.

242. Process. The furnace is charged through the side doors with impure copper in the form of cakes or ingots. By hand this is a slow process, but with mechanical charging as high as 150 tons of cathodes have been charged in two hours by two men. After the furnace is charged, the side doors are closed and luted into place, the temperature of the furnace is raised, and the charge of copper is melted down as quickly as possible. This takes from seven to twelve hours.

The bath is then given an oxidizing fusion. This volatilizes Zn, Pb, and a part of the As and Sb, scorifies Mn, Fe, Pb, Zn, Bi,

and some Cu, and saturates the copper with Cu_2O. The slags as they are formed are skimmed off and saved for re-treatment, since they contain considerable copper. At this stage in the process, in order to hasten oxidation, air is blown through the copper by inserting an iron pipe into the bath. The surface of the slag is further broken and exposed to the air by flapping (striking with a rabble blade). At this stage the copper will contain about 6 per cent Cu_2O. This is called the fining or flapping stage and will require from two to six hours, according to the character of the copper and the nature of the refining process.

The next step in the process is called poling. The object of this is to reduce the percentage of Cu_2O in the set copper and bring it to tough pitch, when it is in the highest degree malleable and ductile. The bath is cleaned of slag and the side doors tightly sealed. Through the skimming doors poles of green wood, from 6 to 10 inches in diameter at the butt and from 15 to 25 feet long, are inserted in the bath of molten metal. These are pushed in as fast as they are burned. The heat of the bath serves to char the wood and to set free H_2O, CO, H, and various hydrocarbons which serve to agitate and stir the bath. The CO, C, and H reduce the oxides of copper to metallic copper. The progress of the reduction has to be closely watched, for if the copper has too little Cu_2O it will be brittle. This is best judged from the appearance of the fracture of a test ingot chilled in water and broken with a sledge. The structure of the fracture of such an ingot, with set copper, is columnar and coarse. Then, as the oxygen content decreases, the structure passes through the stages of cubical and coarse, coarse granular, and at last finely granular and fibrous. The color, at first a dark brick red, becomes a lighter brick red and shades off into a rose color. The luster, at first absent, appears in the form of tiny specks of silkiness, which increase in size until finally the entire surface has a silky appearance. If the reduction is carried too far, the copper (overpoled) becomes porous and brittle, and yellowish in color, and has a brilliant luster. The elimination of impurities in the process is indicated in Table XXIII.

When the copper has "come to nature," or arrived at the tough-pitch stage, it is cast into ingots, wire bars, cakes, slabs, or billets weighing from 10 to 100 pounds. The casting tempera-

ture ought to be low, as a high temperature causes rising in the mold. Copper was formerly cast by hand, but today, in large plants, mechanical casting is the rule. Both the Walker (turn-table) and Repath (straight-line) machines are used.

TABLE XXIII. ELIMINATION OF IMPURITIES IN FIRE REFINING

	Blister Copper	After Melting	After Fining	After Tough Poling
	Per Cent	*Per Cent*	*Per Cent*	*Per Cent*
Cu	98.140	98.950	98.550	99.300
Ag	0.011	0.010	0.010	0.009
Pb	1.060	0.330	0.160	0.170
Ni	0.610	0.350	0.350	0.360
As	0.058	0.058	0.055	0.054
O	0.121	0.302	0.875	0.107

It should be noted that if the copper contains Au or Ag none of this is removed in the fire-refining process. If small in amount they may be left in the copper, since they do not detract from its valuable properties in any way. If they are present in sufficient quantity to warrant their recovery, this can be accomplished only by electrolytic refining.

ELECTROLYSIS OF COPPER

243. General. The aim of the electrolytic refining of copper is to produce a very pure grade of copper by eliminating As, Sb, Bi, and Fe. These are not completely removed by the fire-refining process. With care almost chemically pure copper can be made. When $CuSO_4$ is dissolved in a weak solution of H_2SO_4 it is dissociated into Cu^+ and SO_4^- ions. If this solution is electrolyzed, the SO_4^- ions migrate to the anode and give up their charge; the Cu^+ ions migrate to the cathode, give up their charge, and are deposited as pure metallic copper. In practice anodes of impure copper and cathodes of pure copper are suspended in a tank full of electrolyte of the proper strength. Under the action of the current, copper goes into solution from the anode and is deposited on the cathode. The impurities either are left behind on the corroded anode, pass into solution in the electrolyte, or drop to the bottom of the tank as a slime or mud.

244. Tanks. Both the series and multiple processes are in use, although the former is found in but one American refinery. In the multiple process which is illustrated in Fig. 87 the anodes and the cathodes are connected in multiple and suspended crosswise in a tank of electrolyte. In the series system, illustrated diagrammatically in Fig. 88, electrodes of high-grade copper are placed vertically in series in an electrolyzing tank so as to fit closely into slots in the sides of the tank. As the current passes through the tank the electrodes, with the exception of those at the ends, become negatively charged on the sides facing the entrance and positively charged on the sides facing the exit of the current. The current causes Cu to be dissolved from one side of an electrode and deposited on the negative side of the next following electrode. The first electrode is solely anode and the last electrode is solely cathode.

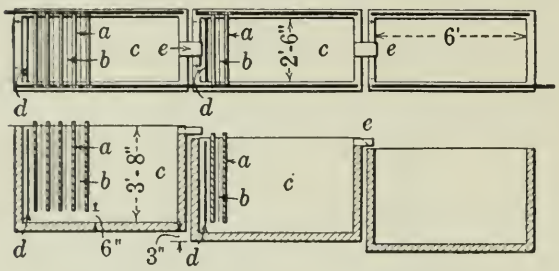


FIG. 87. A multiple system

Since the multiple process is the more common, only that will be described. The details of a tank are shown in Fig. 89. Each tank holds 28 anodes and 29 cathodes and is about 13 feet long. The anodes are about 2 feet by 3 feet and weigh as much as 700 pounds. They are cast with two shoulders, or lugs, so that they can be suspended from the bus bars running along the sides of the tanks. The starting sheets (cathodes) are thin sheets of pure copper. In order to make the proper electrical circuit, as shown in Fig. 89, one end of the cathode and of the anode must be insulated from the bus bar on which it rests by a piece of paraffin-soaked wood or a piece of plate glass.

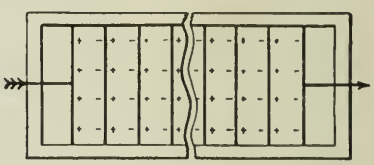


FIG. 88. A series system

245. Behavior of the impurities. The most common and troublesome impurities in blister copper are As, Sb, Bi, Pb, Au, and Ag.

Arsenic is dissolved as $As_2(SO_4)_3$ and may be more or less decomposed by hydrolysis. As_2O_3, being only slightly soluble, falls out of solution and goes into the mud. It is aimed to keep the As

content of the electrolyte below 1.25 per cent, for it has been found that with a difference of potential of 0.3 volt, a current density of from 15 to 20 amperes per square foot, and the bath at a temperature of from 40 to 50° C., As will be plated out with the Cu when the As content reaches 2 per cent. With small amounts of As nearly all of it is precipitated along with the other impurities and goes into the mud.

Antimony behaves in a manner similar to As, but is less readily deposited. In the tanks some dark, insoluble antimony

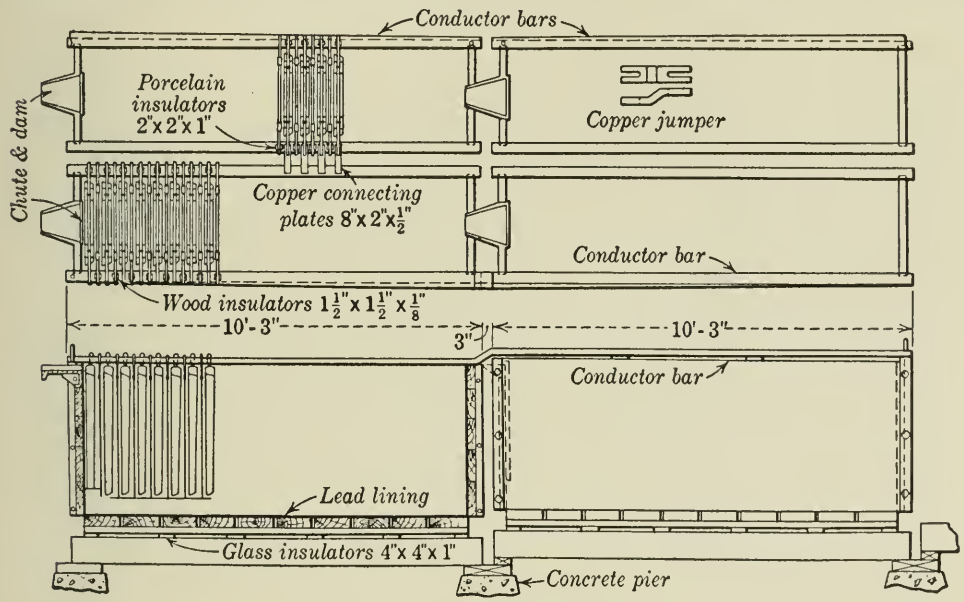


FIG. 89. An electrolytic tank

compound floats about on the surface of the electrolyte and may be entrapped in the Cu as it is deposited.

Bismuth is more readily deposited than As, but usually occurs in such small quantities in the ores as not to interfere seriously with electrolysis.

Lead is converted into $PbSO_4$, which is nearly insoluble in the electrolyte and goes wholly into the anode mud.

Silver, gold, and platinum are not dissolved under normal conditions of electrolyte and go wholly into the slime. Any Ag found in the cathode has been carried to it mechanically.

246. Anodes. The anodes are cast from blister copper. Some care must be taken in their preparation in order to keep down the formation of scrap. The percentage of impurities must be small and the pitch of the copper correct, or else the anode will

be corroded unevenly. For this reason anodes cast directly from the converter are not so desirable as those from the fire-refining process. An anode (from 1 to 2 inches thick) is expected to be corroded in from two to six weeks.

If the impurities are excessive or unevenly distributed, or if the pitch of the copper is too high, the anode will not be evenly corroded. It will become honeycombed, even spongy, and small pieces of the metal will drop off to contaminate the mud in the bottom of the tank. Such partly corroded anodes must be removed and new ones substituted in their place, or the current efficiency will be very low. This material is called scrap and amounts to from 10 to 15 per cent, by weight, of the original anode. This scrap is returned to the refining furnace to be recast into new anodes.

247. Cathodes. The cathode, or starting sheet, is a thin sheet of pure copper. In some plants these are made from commercial sheet copper; but since these make rather expensive cathodes, most large refineries prepare their own by electrolysis. A sheet of rolled copper about $\frac{1}{4}$ inch thick is greased, sprinkled with graphite, and suspended in the depositing tank with the usual anodes. When the deposit is about $\frac{1}{16}$ inch thick it is stripped off with a chisel and this thin sheet is used as a cathode. In order to give these sheets sufficient mechanical strength it is necessary to plate out the Cu very slowly; so the deposition is carried on in special tanks, not with the other cathodes. The starting sheet is suspended by clips from a copper rod about 1 inch in diameter. This rod is flattened at the ends in order to make a good electrical connection with the bus bars of the tank. After from seven to fourteen days of electrolysis the cathodes of a tank are removed by an overhead traveling crane (as indicated in Fig. 90), washed, and sent to the melting department to be fire-refined and cast into the proper shape. Electrolytic copper, while very pure, is not in proper shape for use in industry. In order to be in the highest degree malleable and ductile it must contain a small quantity of Cu_2O; so even electrolytic copper must be fire-refined in order to bring it to the proper pitch.

The electrode distance is usually from 4 to $4\frac{1}{2}$ inches, center to center of anodes. If this distance is too small, fragments of copper, growths, anode mud, etc. tend to bridge the space and cause short circuiting; if too large, there is an unnecessary

increase in resistance, less Cu is deposited, and the electrical energy is dissipated as heat.

248. Electrolyte. The electrolyte should contain from 3 to 4 per cent of Cu, and from 10 to 16 per cent of free H_2SO_4. If the Cu content falls below 2.5 per cent, there is danger of plating out As; if the H_2SO_4 is too high, the bath is decomposed electrically and polarization sets in with a corresponding loss in electrical efficiency. The temperature of the bath ranges from 40° to 60° C. The hotter the bath, the lower the resistance and the smoother the cathode deposit, within the limits just given.

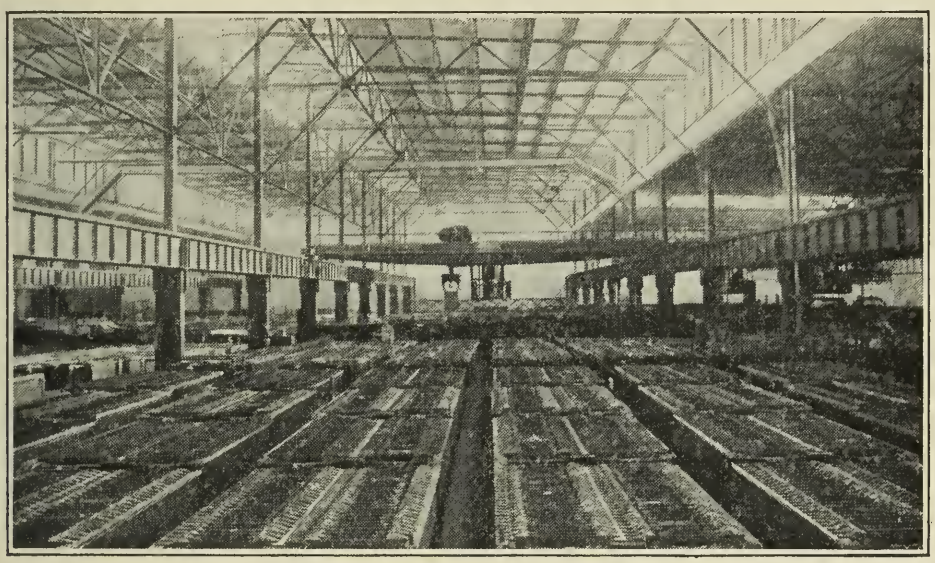


FIG. 90. A tank house — copper-refinery cell room

Courtesy of the Anaconda Copper Mining Company

The tanks are arranged in cascade; that is, with a slight drop between adjoining tanks so that there will be a continuous circulation of electrolyte. This is essential to the correction of differences in composition set up in electrolysis, layering of the bath, and polarization. These, if unchecked, would cause uneven corrosion and a high percentage of scrap. The greater the current density and the higher the temperature, the more rapid the circulation required. It is important, however, to have it slow enough to permit the free settling of the slime which is liberated from the anodes. The usual method of circulation is to have rows of tanks on wide terraces. The spent electrolyte is collected in a main sump, or well, at the foot of terraces, where it is raised by an air lift and returned to the first cells.

In the course of time impurities which are soluble in the electrolyte become so concentrated in it as to interfere seriously with the deposition of the copper. Before such a condition is reached a part of the foul solution is withdrawn and freshly prepared $CuSO_4$ solution is introduced in its place. The principal impurities thus collected are As, Sb, Bi, Ni, and Fe. These may be removed (1) by crystallization, (2) by crystallization and electrodeposition, and (3) by electrodeposition. In (2), which is the most common practice, the solution is heated in lead-lined tanks until it is concentrated to about 42° Bé. and then run into crystallizing pans, where over 80 per cent of the Cu will be separated as $CuSO_4$. These crystals can be used to bring the tank solution up to proper strength or they find a ready market as blue vitriol. The mother liquor left from crystallization may be electrolyzed with sheet-lead anodes and sheet-copper cathodes, and all the remaining Cu deposited. If high enough in As the residue can be treated to recover this.

249. Current. The current density shows a range of from 15 to 25 amperes per square foot. The lower current density prevents even a trace of As from passing to the cathode. The drop in potential between tanks ranges from 0.2 to 0.4 volt. Theoretically 1 ampere hour deposits from a $CuSO_4$ solution 1.186 grams of Cu, or 382.4 ampere hours are required in order to deposit 1 pound of Cu; practically it requires from 400 to 500 ampere hours. It is essential to keep the contacts bright in order to retard corrosion and prevent creeping of the electrolyte, with consequent loss of current.

250. Anode mud. During electrolysis a black slime or mud collects in the bottom of the tanks. The composition of this mud varies considerably with the character of the anodes. Table XXIV indicates the range in composition. This residue amounts to from 1 to 3 per cent of the weight of the original anodes. When it has collected in sufficient quantity, the electrolyte is siphoned from a cascade of tanks and the residue flushed out and worked down from the top to the bottom tank, where it is removed. It is then screened through a 40-mesh screen in order to remove metallic particles and refuse which may have fallen into the tanks during electrolysis. This slime is then thoroughly washed, filter-pressed, and dried. In general there are three ways of treating it to recover the precious metals.

TABLE XXIV. ANALYSES OF ANODE MUD

	GREAT FALLS	NEW JERSEY	BALTIMORE
Cu	14.80	12.26	11.01
Ag	57.00	53.68	53.89
Au	—	0.28	0.30
Pt	0.0001	—	—
Pb	5.26	3.58	0.91
Sb	2.00	6.76	6.25
As	2.60	5.42	2.11
Bi	5.70	0.45	3.93
Ni	—	0.30	—
Co	0.006	—	—
Fe	—	0.14	—
Zn	0.09	—	—
Se	2.0	2.30	0.39
Te	1.0	3.56	1.17

In direct smelting the dried cake is charged into a small reverberatory furnace with soda ash and siliceous ore in such proportions as to produce a suitable slag, and the mixture is given an oxidizing fusion. From this fusion come slag, flue dust, and bullion. The slag and flue dust are returned to the process, the bullion (containing the gold, silver, and some impurities), from 820 to 860 fine, is usually sent to the mint for refining. This method is not applicable to very impure slimes and is not considered good practice today.

In lead soaking the dried slime is charged, in paper bags containing from 10 to 15 pounds each, onto the lead bath of a cupeling furnace. The silver and gold are dissolved in the lead, while the cupeling process oxidizes and scorifies most of the other impurities.

A third process involving roasting and leaching is in common use for slimes high in copper. In this the dried cake from the filter presses is given an oxidizing fusion in a reverberatory furnace, at from 300° to 400° C., for about twelve hours. This converts the copper into CuO and volatilizes some of the As, Sb, and Zn. This roasted product is then leached in lead-lined tanks with hot H_2SO_4 solution (15 per cent). The Se and Te are removed by passing the solution over metallic copper, and the purified solution is returned to the tank house. The residue from the acid treatment, usually containing less than 1 per cent Cu, may be treated by lead soaking, but the more common

method at refining plants is to smelt the dried material in a small reverberatory furnace with suitable fluxes. The slag from this fusion goes back for re-treatment, and the bullion running from 820 to 860 fine is sent to the mint for refining.

251. Multiple versus series. The following advantages are claimed for the multiple system: (1) Anodes with over 1 per cent of combined impurities and up to 1000 ounces of Ag and Au per ton can be treated, whereas in the series, owing to the fact that the anodes have to be carefully prepared by rolling, the copper should not contain over 0.17 per cent of combined impurities or 100 ounces per ton of Ag and Au. (2) The electrodes and the anode scrap are easily handled by mechanical devices in the multiple system. In the series this must be done largely by hand. (3) In the multiple system the large electrode distance and the open spaces about the sides of the electrodes favor circulation of the electrolyte without stirring up the mud.

The following advantages are claimed for the series system: (1) The electrode distance ($\frac{7}{8}$ inch) is smaller, so that the fall in potential is only from 0.15 to 0.30 volt. This means that only half or two thirds of the power will be required to deposit a given amount of copper. (2) In the series system a large part of the copper in the bus bars is saved. With average copper bullion the interest on the metal thus locked up is about half of that in the multiple. (3) The scrap produced in the series system is from 3 to 8 per cent as against 10 and often 15 per cent in the multiple system. (4) The series system formerly required less floor space than the multiple, but this has been corrected in the newer plants by using larger electrodes in the multiple system.

The fact that all the refineries in the United States except one are operating with the multiple system seems to indicate that on the whole it is the most satisfactory process.

HYDROMETALLURGY OF COPPER

252. General. Hydrometallurgical treatment, or leaching, is any process whereby the valuable metal or metals are recovered by means of some lixiviant, or solvent, leaving the gangue, or waste matter, practically unaffected. From the solution the valuable metal can be precipitated in a relatively pure form.

Such processes are often termed wet in contrast to the dry, or smelting, methods. Leaching has been practiced for a number of years on ores of gold and silver, but only during the last decade have metallurgists been able to perfect methods for the treatment of ores of copper, zinc, and lead. Today it is estimated that fully 15 per cent of the world's output of copper is obtained by leaching processes. Such processes are making very rapid strides, — so much so that one prominent metallurgist makes the unqualified statement that the day of the smelter has passed.

253. Advantages of leaching. The advantages of this method of treating copper ores are many, among them the following:

1. By electrodeposition the copper can be obtained directly and in a very pure form.

2. Siliceous gangue is unaffected by most solvents, while in all smelting processes this silica must be slagged with relatively expensive fluxes.

3. The handling of the products (by pipes or conveyors) is much cheaper and easier than the handling of molten mattes, slags, and blister copper.

4. Lower-grade ores can be worked at a profit.

Unfortunately, in the present state of the art, it is not applicable to all ores, for there are roasting and chemical problems as yet unsolved by our metallurgists.

254. Solvents. The following reagents have been proposed as solvents of the copper minerals. The order given is about that of their importance at present: (1) sulphuric acid; (2) ammonia and ammonium carbonate; (3) ferric sulphate; (4) sulphur dioxide; (5) ferric chloride; (6) cupric chloride; (7) hydrochloric acid; (8) chlorine; (9) nitric acid.

Sulphuric acid, because of its cheapness, is the solvent most commonly used. It has distinct disadvantages, however, among them being the fact that it does not dissolve sulphide copper minerals and does dissolve many of the common impurities. In dilute solutions, however, it has a selective action on copper, dissolving it in preference to other constituents.

Ammonia and ammonium carbonate, in the presence of air, will dissolve metallic copper and copper oxides. It cannot, however, be used with the more common sulphide minerals.

Ferric sulphate has the advantage of being an active solvent

of copper sulphide. Excess ferric sulphate is detrimental to electrodeposition, so that the removal of this frequently offers a perplexing problem.

Sulphur dioxide, dissolved in water as sulphurous acid, is an active solvent of most oxidized copper compounds. It has the advantage of being cheaply and easily obtained from local pyrite.

The rest of the solvents, while often very active ones, have been abandoned as too expensive or too difficult to handle on the large scale which is necessary in treating low-grade ores. The reactions involved in the use of the above solvents are as follows:

$$CuO + H_2SO_4 = CuSO_4 + H_2O,$$
$$CuO + (NH_4)_2CO_3 = CuCO_3 \cdot 2\,NH_3 + H_2O,$$
$$Cu_2S + Fe_2(SO_4)_3 = CuS + CuSO_4 + 2\,FeSO_4,$$
$$CuS + Fe_2(SO_4)_3 = CuSO_4 + 2\,FeSO_4 + S,$$
$$3\,CuO + Fe_2(SO_4)_3 = 3\,CuSO_4 + Fe_2O_3,$$
$$3\,CuO + 3\,SO_2 = 3\,CuSO_3,$$
$$3\,CuSO_3 + CuO = Cu_2SO_3 \cdot CuSO_3 + CuSO_4.$$

255. Precipitation. The copper is always obtained in the form of an aqueous solution of some salt. As such it has no value or use, and hence the metal must be precipitated. This can be accomplished in many ways, but the most practical precipitants are the following: (1) electrolysis; (2) metallic iron; (3) hydrogen sulphide; (4) heat.

Precipitation by electrolysis is carried out in much the same way as in the refining of copper, except that it is necessary to use insoluble anodes and sometimes a different arrangement in the tank. The development of a satisfactory anode has been slow; lead, magnetite, silicon-lead, and ferrosilicon have been suggested and used. The use of insoluble anodes involves the use of a great deal more current to effect the decomposition of the copper salt, — roughly ten times as much current as in the multiple system of refining, as indicated below:

Insoluble electrodes . . .	0.8 pound of Cu deposited per kilowatt hour
Multiple system	8.0 pounds of Cu deposited per kilowatt hour
Series system	14.0 pounds of Cu deposited per kilowatt hour

The solution is not under as good control as in the refining process, so that undue quantities of ferric sulphate or impurities often get into the solution. The former is particularly bad,

since it redissolves the copper as indicated below and lowers the current efficiency:

$$Cu + Fe_2(SO_4)_3 = 2\ FeSO_4 + CuSO_4.$$

Iron has always enjoyed considerable popularity as a precipitant, owing to the fact that it is cheap, easily obtainable in the form of scrap, and simple to use. The reactions which go on in the case of sulphate solutions are the following:

$$CuSO_4 + Fe = Cu + FeSO_4,$$
$$Fe_2(SO_4)_3 + Fe = 3\ FeSO_4,$$
$$H_2SO_4 + Fe = FeSO_4 + 2\ H.$$

The precipitated copper (seldom over 90 per cent pure) is known as cement copper. Theoretically it requires only 0.878 pound of iron to precipitate one pound of copper, but the consumption, owing to the above reactions with H_2SO_4 and $Fe_2(SO_4)_3$, is usually from 1.5 to 2.0 pounds. Often, however, because of low copper concentration or high impurities, the solution must be treated in this way. Sponge iron, produced by the reduction of high-grade iron ore by CO gas, has recently been used in place of scrap. It is more expensive, but, on the other hand, it is far more efficient, owing to its porous nature, and the solution can be agitated during precipitation, — a distinct advantage.

H_2S offers a complete and efficient precipitation:

$$CuSO_4 + H_2S = CuS + H_2SO_4.$$

It is expensive to manufacture and handle, and has the distinct disadvantage of leaving the copper in a form that requires smelting.

Cuprous-cupric sulphite (from the SO_2 process) and copper ammonium carbonate (from the ammonia process) are easily decomposed by heat and the copper oxide recovered as a high-grade precipitate.

256. Roasting. Copper oxide and many other oxidized copper compounds are easily dissolved by water or dilute sulphuric acid. The sulphide minerals are not dissolved, and unfortunately the bulk of our copper deposits are in this form. Roasting, of course, if properly conducted, will oxidize these compounds; but this is a long, uncertain, and expensive operation, and there is the attendant difficulty of flue dust and fume. It is

probably safe to say that this difficulty, more than any other, has held back the progress of the leaching of sulphide copper ores. Today very few of the processes which involve roasting are in common use.

257. Washing. Another difficulty in hydrometallurgical treatment is that of washing. If the pulp is drained or even filter-pressed there is a considerable amount (from 20 to 50 per cent of the total copper) of copper-bearing solution left in the interstices of the ore. The profitable recovery of this is a problem, for if the material is washed with water until the copper content has been reduced to the desired minimum, the bulk of the solution is very large, and, furthermore, the copper content of the wash has been so reduced as to render the precipitation difficult or even impossible. Evaporation of the excess water is of course out of the question on account of the cost.

258. Practice. The present state of the art is such that most of the processes are still in the laboratory or pilot-plant stage. A discussion of these and their problems in this text would seem rather unprofitable, and the author believes that the student will derive more benefit from a brief study of two of the really successful commercial processes. We will take as examples the plants of the New Cornelia Copper Company and the Kennecott Copper Corporation.

THE NEW CORNELIA COPPER PROCESS

This plant, at Ajo, Arizona, has a capacity of about 5000 tons per twenty-four hours. For the purposes of this discussion we will divide the process into the following steps: (1) crushing; (2) leaching; (3) reduction of the iron; (4) electrolysis.

259. Crushing. The ore is mined by means of steam shovels in pieces up to the largest size that can be conveniently handled. The material is then crushed, first in gyratories and then in Symons disk crushers, to pass a $\frac{1}{4}$-inch screen. This material is then taken on conveyor belts to the leaching tanks.

260. Leaching. The leaching tanks are of reënforced concrete with wooden filter bottoms and hard-lead sides and launders. Both sides and bottom are provided with shoveling strips to protect the lead from abrasion. Each tank ($88 \times 88 \times 17$ feet) will hold 5000 tons of crushed ore. The solvent used is a dilute

solution of sulphuric acid. The countercurrent system is used, the solution in each tank being circulated by means of centrifugal pumps. Leaching occupies from six to eight days. After the rich solution is drained off, the contents are washed four times with water. These washings are advanced each time; that is, the fourth wash of one leach will be used as the third wash of the next, and so on until it contains enough copper to be sent on to electrolysis. The tailings are removed by means of a Hewlett unloader.

261. Reduction of the iron. It is a well-known fact that the electrodeposition of copper from dilute sulphuric acid solutions containing iron is inefficient. The iron, by its alternate oxidation and reduction, will consume considerable electric energy. Several methods have been tried out to get around this difficulty, but the reduction by SO_2 has been most successful. The expense and difficulty of this reduction is one of the disadvantages of the whole process. The SO_2 is obtained by roasting high-sulphur, low-copper ores in Wedge furnaces and cooling this gas with water in lead-lined spray chambers. The reduction of the ferric sulphate is carried out in a series of towers 20 feet in diameter by 40 feet in height. The reaction involved is as follows:

$$Fe_2(SO_4)_3 + SO_2 + 2\,H_2O = 2\,FeSO_4 + 2\,H_2SO_4.$$

These tanks are filled with baffles so as to spread the solution out into as thin a film as possible. The solution to be reduced travels countercurrent to the gas, so that the solution with the least amount of unreduced iron will come in contact with the strongest gas. The extent of the reduction is indicated below:

	Ferrous Iron	Ferric Iron
	Per Cent	*Per Cent*
Solution entering towers	1.01	0.43
Solution leaving first pair of towers	1.05	0.39
Solution leaving third pair of towers	1.42	0.02
Solution leaving settling tank	1.44	0.00

262. Electrolysis. Electrolysis is carried out in lead-lined tanks somewhat similar to those used in the refining of copper. The electrodes are arranged differently. There are 84 anodes and 77 cathodes in each tank, the electrodes hanging parallel to the flow of solution. The anodes are of hard lead, measure

$40 \times 51 \times \frac{1}{4}$ inches, weigh about 215 pounds, and have a life of over a year. The cathodes are starting sheets weighing 17 pounds at the beginning of electrolysis and about 140 pounds at the finish. The cathode copper ranges in purity from 99.2 to 99.9, most of the impurities being mechanically entrained slimes. The drop in potential between anode and cathode is 2 volts, and the current density about 8 amperes per square foot of cathode surface. The current efficiency (ordinarily about 80 per cent) depends upon the quantity of ferric sulphate that is present owing to the reactions between ferric sulphate and metallic copper, as indicated below:

$$Cu + Fe_2(SO_4)_3 = CuSO_4 + 2\ FeSO_4.$$

A part of the solution must be discarded each day, or else the impurities become so concentrated as to interfere with electrolysis. It has been found that the iron content is indirectly a measure of these impurities. When the iron content of the solution is less than 2 per cent, no trouble is experienced. The copper from this discarded liquor is recovered by cementation on scrap iron.

THE KENNECOTT PROCESS

263. Ammonia leaching. At this plant de-slimed tailings containing about 1.50 per cent of Cu, of which about 85 per cent is in soluble form as copper carbonate, are treated by the ammonia leaching process.

The leaching tanks are of steel, 30 feet in diameter and holding about 500 tons each. They are provided with a tightly fitting, dome-shaped cover. When the tanks have been filled, the first leaching solution (rich copper ammonia solution from a previous leach and concentrated ammonia) is run in at the bottom of the tank and in rising through the crushed ore displaces any moisture that may be present. The rich solution is then added at the top and leaches downward through a filter bottom. A centrifugal pump maintains the circulation as long as there is any extractable copper left, — usually for about thirty hours. This solution (containing about 4.5 per cent of Cu and 7.5 per cent of NH_3) is then drawn off and sent to the evaporators. The contents of the tank are then washed, first with weak copper ammonia solution and then with steam, until

the vapor from the tank contains less than 0.5 per cent of NH_3, when the tanks are emptied.

In the evaporators the ammonia vapor is drawn off to be returned to the process, while the Cu_2O falls out of solution to the bottom of the evaporator. This precipitate is removed from time to time and passed to filter presses, which yield a product averaging about 80 per cent Cu.

CONCENTRATION OF COPPER ORES

264. Low-grade ores. Most of our copper at the present time is derived from ores so low-grade that direct smelting is out of the question. Many of our large plants are operating on ores containing less than 2.5 per cent of Cu by concentrating these ores into products containing 20 per cent or more of copper and then smelting these. A flow sheet of the plant of the New Cornelia Copper Company is given in Figs. 91 and 92 to show the application of the principles of concentration already outlined under "Preparation of Ores." By this means, from an ore containing 1.421 per cent of Cu, 89.166 per cent of the contained copper is recovered in the form of a concentrate containing 29.65 per cent of Cu.

NEW CORNELIA CONCENTRATING MILL

265. Crushing. The New Cornelia Copper Company at Ajo, Arizona, has a concentrating mill treating about 5000 tons of copper ore per day. This plant is a good example of a modern water-gravity concentration and flotation mill. It embodies many distinctive features of design, which are more fully described in an article by the designer, H. Kenyon Burch, in *Engineering and Mining Journal-Press*, Vol. 118, No. 21. A flow sheet of this plant is given in Figs. 91 and 92. The crushing is carried out in a separate plant which delivers a $\frac{5}{8}$-inch product to the mill bins. This was made necessary by the fact that the mine produces two classes of ore, a leaching and a smelting grade. Both of these require about the same degree of crushing, so that one crushing plant serves both ores, although by so doing a rather elaborate conveyor system is made necessary. In general this preliminary breaking, a flow sheet of which is shown in

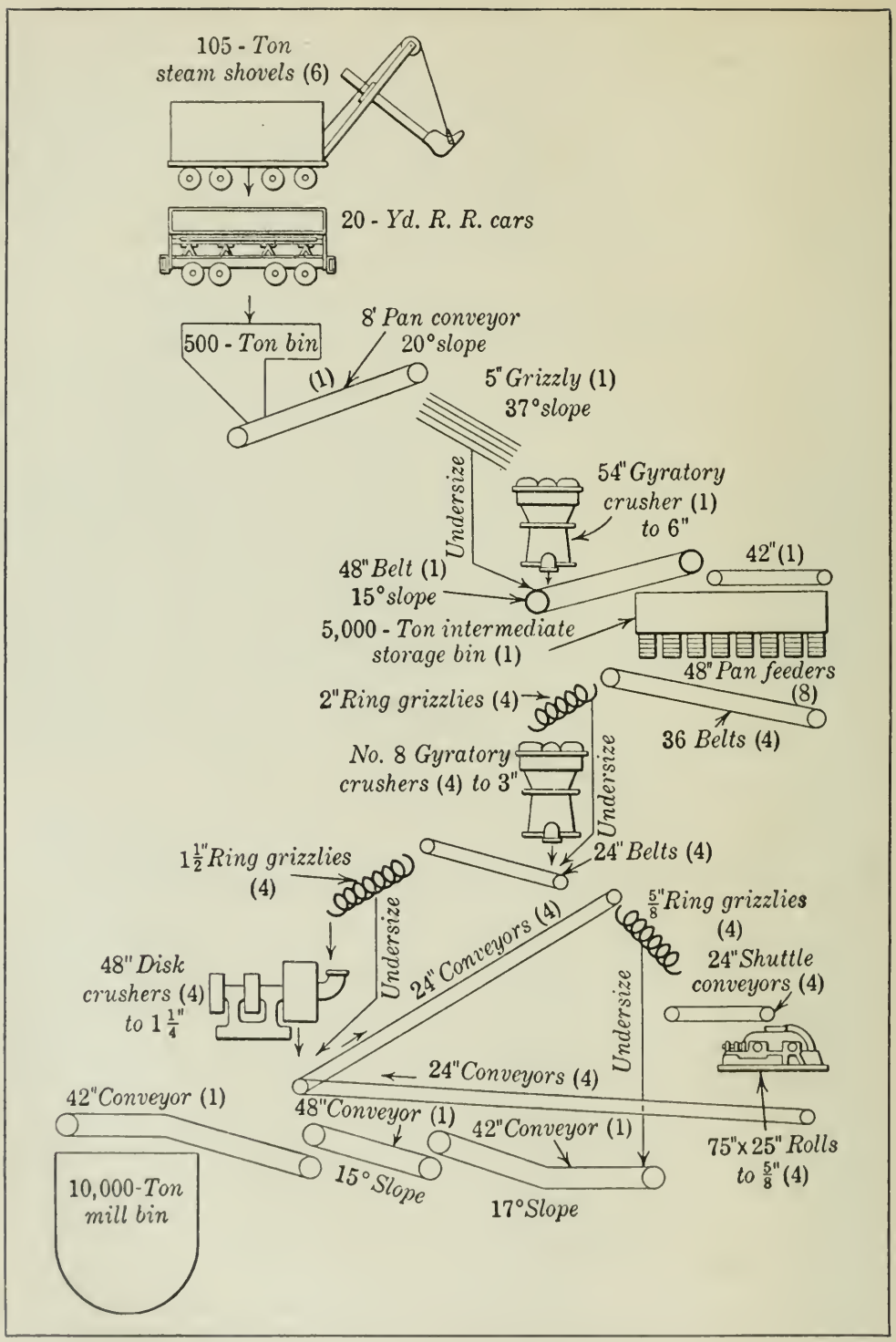


FIG. 91. The New Cornelia crushing plant

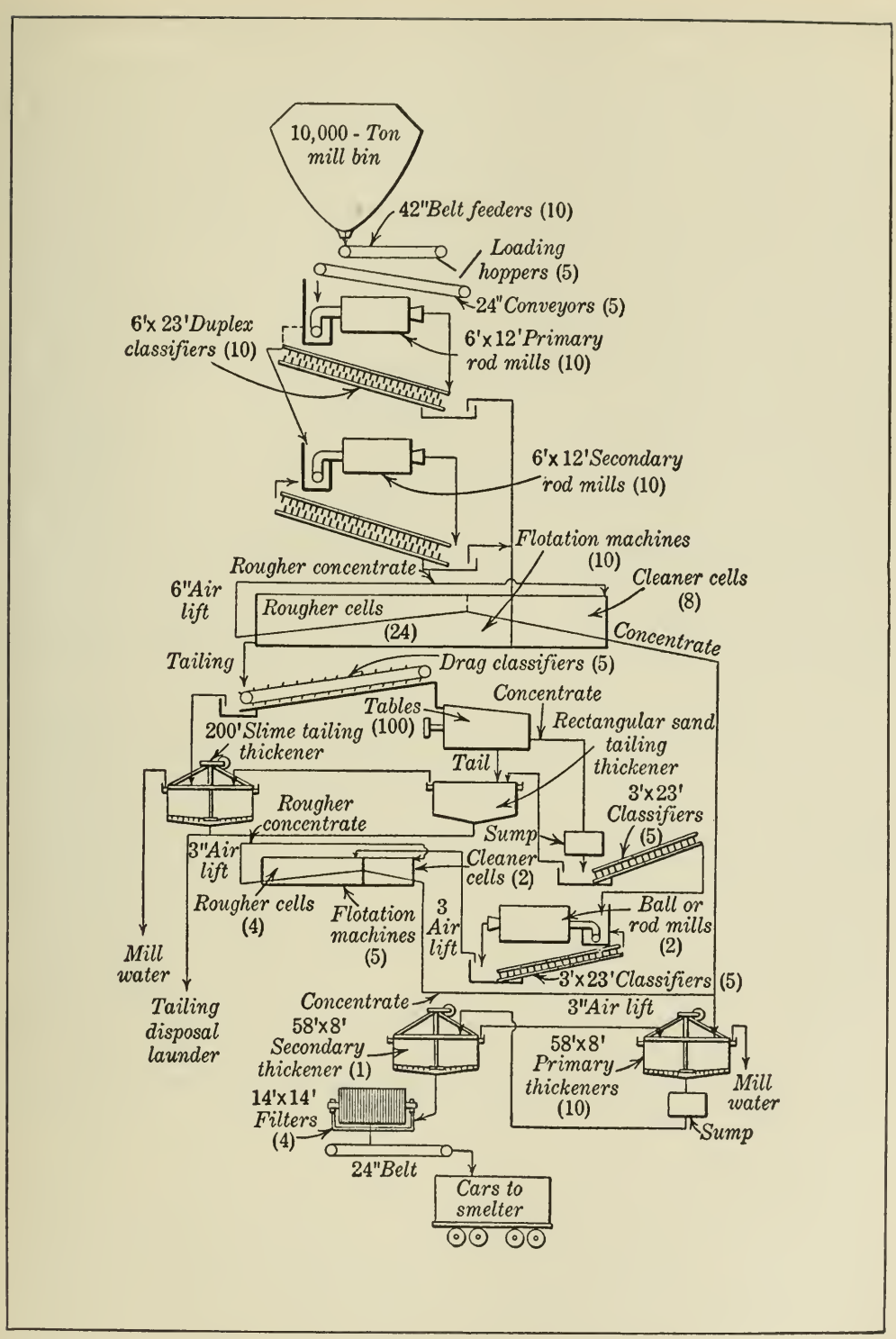


FIG. 92. The New Cornelia concentrator

Fig. 91, is carried out in primary and secondary gyratory crushers, 48-inch Symons disk crushers, and 78 × 25 inch rolls.

266. Grinding. The mill bin is of the suspension-bunker type, with a capacity of about 33 tons per lineal foot of length. Discharge hoppers with belt feeders are spaced 10 feet apart. Two feeders discharge upon a 24-inch conveyor equipped with a weightometer and delivering to the two primary rod mills of each section. The mill is divided into five units, or sections, so that one or more of these may be shut down without interfering with the operation of the plant as a whole. There are two primary and two secondary rod mills in each section. These are of the open-end type, 6 × 12 feet, and carry a normal rod charge of 23 tons. High-carbon steel rods 3 inches in diameter are fed into the mill and usually wear down to about $\frac{5}{8}$ inch in diameter before being ejected. Each mill delivers its product to a 6 × 23 foot Dorr duplex classifier, the primary classifiers being arranged to return all or a part of their sand to the feed end of the primary mill. The overflow of the secondary classifiers goes directly to the oil-flotation department.

267. Oil flotation. There are two flotation machines (Inspiration type) in each unit. Each flotation machine has 24 rougher pans and 8 cleaner pans. The flotation rougher concentrate is returned to the cleaner cells by a 6-inch air lift. Provision is made for combining the concentrate from the first few roughers with that coming from the cleaner cells, as it is found that part of the rougher concentrate does not require cleaning. The flotation tailing goes to a drag classifier. The overflow of this classifier goes to the slime-tailing thickener, the sand to 20 tables for treatment. The tailings from the concentrating tables go to the sand-tailing thickener and the concentrate to a sump, from which they are pumped to the regrinding plant for re-treatment.

268. Regrinding. The regrinding equipment consists of a ball mill and a rod mill, either of which has ample capacity for the whole plant. These work in closed circuit with a 3 × 23 foot Dorr classifier. The overflow of this classifier is elevated by a 3-inch air lift to a flotation machine with a four-pan rougher and a two-pan cleaner compartment. The concentrates from the cleaner join the main flotation concentrates and go to the primary thickeners. There are two 58 × 8 foot thickeners for

each section of the concentrator. The overflow of these goes to the return-water sump and the thickened concentrate to a secondary 58 × 8 foot thickener. The overflow of this goes back to the primary thickener, and the spigot to Oliver filter presses.

269. Filter pressing. The filter plant consists of four 14 × 14 foot Oliver filter presses. The cake drops to a 24-inch conveyor belt discharging directly into cars for shipment to the smelter. The tailing-sand thickener is a rectangular concrete tank 20 × 60 feet in plan, having a sloping bottom with classifying cones. The overflow from this joins the overflow from the drag classifiers, for dewatering in a 200-foot secondary tank thickener, the sand going directly to tailings disposal, joining the sand from the 200-foot thickener. The overflow from the secondary tank is returned to the mill for use. The sand from the 200-foot thickener is sent to the tailings-disposal site of 250 acres, where a little more water is recovered and sent back to the mill.

Table XXV gives metallurgical data covering the recent operation of this plant.

TABLE XXV. METALLURGICAL DATA FROM THE NEW CORNELIA COPPER COMPANY (1927)

Tons treated	2,298,666
Ratio of concentration	23.328
Feed, per cent Cu	1.421
Feed, ounces of Au per ton	0.011
Feed, ounces of Ag per ton	0.114
Tails, per cent Cu	0.161
Concentrates, per cent Cu	29.65
Recovery of Cu (in per cent)	89.166
Per cent on 65-mesh feed	16.3
Gallons of water per ton of ore treated	280.04
Power consumed per ton of ore milled (in kilowatt hours)	14.700

THE UNITED VERDE SMELTER

270. Crushing and handling. The plant of the United Verde Copper Company, at Clarkdale, Arizona, is a good example of a large modern copper smelter. A generalized flow sheet* of this plant is shown in Fig. 93. With a labor force of about 375 men this smelter handles each day about 3500 tons of ore,

* See *Engineering and Mining Journal-Press*, Vol. 118, No. 3.

175 tons of limestone, 85 tons of coke, and 300 tons of coal, besides a large tonnage of intermediate products such as calcines, flue dust, converter flux, and slag, — a total tonnage of about 13,000.

The ore is received from the mine in 75-ton cars and dumped into the receiving bins of the crushing plant or into the coarse-ore bins of the smelter. The crushing plant delivers a coarse

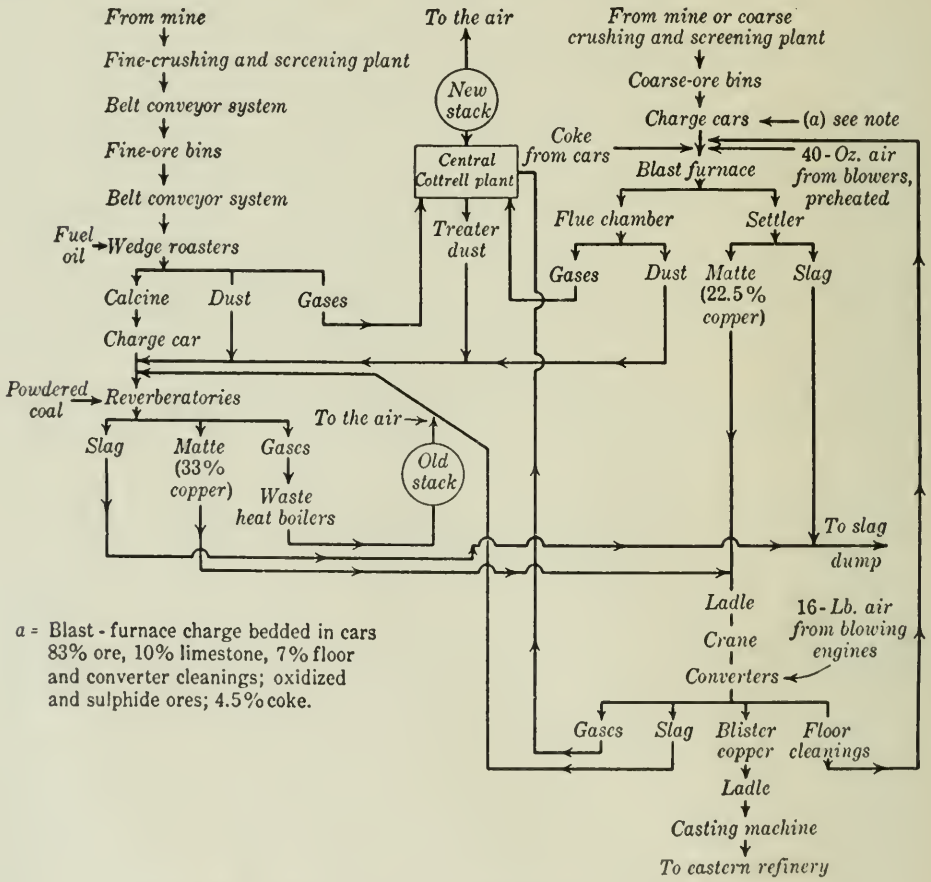


FIG. 93. A flow sheet of the United Verde smelter

product to the coarse-ore bins or a $\frac{1}{4}$-inch product to the fine-ore bins. From the coarse-ore bins the material, crushed to 3-inch size, passes, by weighing hoppers and charge cars, to the blast furnaces. From the fine-ore bins the material is delivered by a conveying system to the roasters, and thence by electric haulage to the reverberatory furnaces. The coarse-crushing and fine-crushing plants and the stock-pile provide 79,950 tons, and the coarse-ore and fine-ore bins, 24,000 tons, storage of ore and limestone. The fuel storage is 12,000 tons of coal, 3000 tons of

coke, 20,000 barrels of fuel oil, and 600 tons of Diesel oil. The approximate analyses of the coarse and fine ore are as follows:

	Coarse Ore	Fine Ore
	Per Cent	*Per Cent*
Cu	5.5	4.8
Insoluble	23.0	28.0
SiO_2	21.2	26.0
Fe	28.6	25.6
Al_2O_3	4.6	6.7
S	27.3	21.8
Zn	1.7	1.5
CaO	1.1	1.0
Ag, ounces per ton	1.84	2.95
Au, ounces per ton	0.05	0.07

271. Blast furnaces. There are four 48 inch × 26 foot blast furnaces. The average amount of material treated per furnace day is 718 tons of charge, or 8 tons per square foot of hearth area. An average of 4.7 per cent of coke is required. The furnaces are blown with air, preheated to about 70° F., and require 70,000 cubic feet per ton of charge. The blast-furnace matte averages 22.5 per cent Cu. The average analyses of blast-furnace charge and slag are as follows:

	Charge	Slag
	Per Cent	*Per Cent*
SiO_2	20	35
Fe	25	39 (FeO)
Al_2O_3	4	7
S	22	—
CaO	7	11
Zn	1.5	2
Cu	5	0.3

Experiments have indicated that by the use of well-screened ore of proper analysis the blast furnaces often average better than 850 tons per day, but with inferior screening the tonnage falls to 700 and the coke consumption increases. Slag is hauled away in motor-tilted slag pots. Matte is discharged from the forehearth by a runner to ladles and thence to the converters.

272. Reverberatories. There are twelve 6-hearth, 21.5-foot and twelve 7-hearth, 22.5-foot Wedge roasters. The sulphur in the roasted ore is reduced from 20–24 per cent to 8–9 per

cent. This sulphur furnishes most of the heat for the process. An amount of extraneous heat depending upon the rate of roasting and the sulphur content may be required (0.25 to 4 gallons of fuel oil per ton).

The reverberatory plant consists of three 19 × 100 foot and three 25 × 101 foot furnaces. The average amount treated per furnace day is 560 tons of charge requiring about 20 per cent of coal. These reverberatories are fired with powdered coal, and each supplies two 700-horse-power, waste-heat boilers. Owing to the fact that the normal capacity of the roasters is 1800 tons per day, no more than this can be treated in the reverberatory plant. The blast furnaces are placed end to end and the reverberatories side by side at a level above the converter floor and on one side of the converter aisle. This gives the least transfer distance for handling the matte to the converters. The approximate analyses of reverberatory charge and slag are as follows:

	Charge	Slag
	Per Cent	*Per Cent*
Cu	5.8	0.4
SiO_2	27.0	34.0
Fe	36.5	46.0 (FeO)
Al_2O_3	7.7	8.0
CaO	1.4	2.0
Zn	2.0	2.0

The reverberatory matte averages 33 per cent Cu. In connection with the cost of treatment Mr. George J. Young,* in describing this plant, writes as follows:

Trinidad coke, which is used in the blast furnaces, costs $15 per ton, and at 4.5 per cent of the charge the fuel cost of blast-furnace smelting is $0.675 per ton of charge. Coal from Gallup, New Mexico, costs $5.25 per ton, and when pulverized $6 per ton. Fuel oil from California costs $2 per barrel. The reverberatory fuel costs $1.25 per ton of charge, and the oil fuel for roasting about $0.05 per ton. The approximate fuel cost of reverberatory smelting is $1.30 per ton of charge, not allowing credit for the waste heat recovered. There is thus a small advantage in lower fuel cost for blast-furnace smelting. The copper content of the blast-furnace slag is lower, which gives it a further advantage. However, the power requirements of the smelter necessitate the use of the waste heat, and fine ore can best

* *Engineering and Mining Journal-Press*, Vol. 118, No. 3.

be smelted in reverberatories. Use of reverberatory matte reduces the amount of smelting in the converter and the volume of the converter slag. Thus the reverberatory with its accessory roasters advances the process of reduction farther than the blast furnaces. The practice of the plant favors the use of a greater number of reverberatories and fewer blast furnaces than are at present in operation.

273. Converting. In the converting department there are eight 12-foot-diameter Great Falls converters. Siliceous ore is used as flux, and the process is carried out much as described in the text. Owing to the low grade of the matte the volume of converter slag is excessive. For handling the blister copper two straight-line casting machines are provided. These are placed at the end of the row of converters. The skull breaker is placed near one end of the converter aisle, the other end being utilized for lining and repairing converters.

274. Flue dust. After passing through the waste-heat boilers, the reverberatory gases are discharged into the atmosphere. The blast furnace and converter gases are received in a dust chamber $30 \times 59 \times 220$ feet, provided with hopper bottoms. Under these run two tracks for disposal of the settled dust. The roaster gases are received in a $21 \times 50 \times 140$ foot dust chamber of similar construction. These both discharge the gas (at 400° F.) into a Cottrell-treater plant.

Four treater batteries are arranged in parallel between the inlet and outlet flues. This arrangement permits of the three types being used in parallel or any battery cut out for repairs or cleaning. Two treater batteries consist each of six units containing each one hundred and twenty 12-inch pipes 16 feet in length of the same general type as described on page 177. The third battery, of the plate type, consists of receiving electrodes of vertical plates of corrugated steel, 9 inches apart, placed parallel to the gas flow. The discharge electrodes are $\frac{3}{8}$-inch-square twisted steel rods running longitudinally and spaced 6 inches apart in a vertical plane between each pair of receiving electrodes. The fourth battery, of the transverse pervious electrode type, consists of receiving electrodes of $\frac{1}{4}$-inch pipe 2 inches apart in a vertical plane at right angles to the gas flow, the successive sets of electrodes being 9 inches apart. The discharge electrodes are $\frac{1}{4}$-inch-square twisted steel bars arranged horizontally 6 inches apart in a vertical plane at right angles to the gas flow.

Each battery has a capacity of 200,000 cubic feet of gas per minute. The voltage is maintained at from 50,000 to 75,000 volts, the power requirement is 3900 kilowatt hours per day. The velocity of gases is about 6 feet per second, entering at 400° F. and leaving at 300° F. The amount of dust recovered in the treater is about 40 tons per day, while about 70 tons per day more is recovered from the dust chambers and flues.

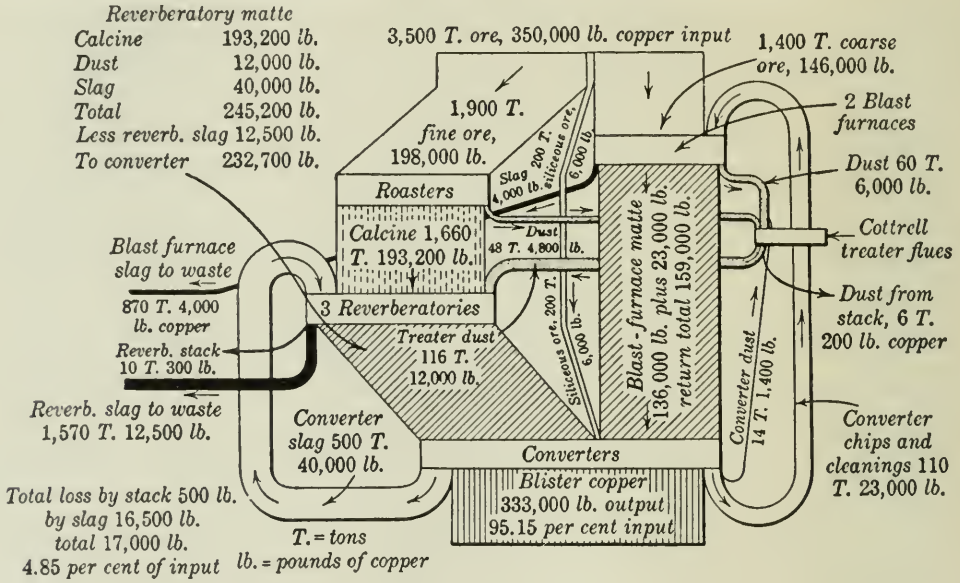

Reverberatory matte
Calcine 193,200 lb.
Dust 12,000 lb.
Slag 40,000 lb.
Total 245,200 lb.
Less reverb. slag 12,500 lb.
To converter 232,700 lb.
3,500 T. ore, 350,000 lb. copper input
1,400 T. coarse ore, 146,000 lb.
2 Blast furnaces
1,900 T. fine ore, 198,000 lb.
200 T. siliceous ore, 6,000 lb.
Slag 4,000 lb.
Roasters
Calcine 1,660 T. 193,200 lb.
Dust 48 T. 4,800 lb.
Dust 60 T. 6,000 lb.
Cottrell treater flues
Blast furnace slag to waste
870 T. 4,000 lb. copper
3 Reverberatories
Blast-furnace matte 136,000 lb. plus 23,000 lb. return total 159,000 lb.
Converter dust 14 T. 1,400 lb.
Dust from stack, 6 T. 200 lb. copper
Reverb. stack 10 T. 300 lb.
Treater dust 116 T. 12,000 lb.
Siliceous ore, 200 T. 6,000 lb.
Reverb. slag to waste 1,570 T. 12,500 lb.
Converter slag 500 T. 40,000 lb.
Converters
Converter chips and cleanings 110 T. 23,000 lb.
Blister copper 333,000 lb. output 95.15 per cent input
Total loss by stack 500 lb. by slag 16,500 lb. total 17,000 lb. 4.85 per cent of input
T. = tons
lb. = pounds of copper

FIG. 94. A daily graphic balance sheet

Fig. 94 shows a diagrammatic balance sheet indicating the proportion of copper in the different products and the larger metallurgical losses.

In Chapter VIII, Fig. 111, will be found a flow sheet of the Tooele smelter, illustrating a slightly different method of treating a copper-bearing ore.

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CHAPTER VIII

LEAD

GENERAL

275. History. Lead was one of the few metals known to the ancient world. This is doubtless accounted for by the ease with which lead can be reduced from its natural compounds. It was probably discovered about 5000 B.C. and was in common use in Egypt in 1500 B.C. Mines worked by the Greeks in Attica before 500 B.C. are still in operation. There is scarcely a country in the world that does not produce a small amount of primary lead. Lead mining in this country dates back to 1621, when lead ore was mined and smelted in Virginia. At present the United States is the world's largest producer of this metal.

276. Physical properties. While isolated specimens of metallic lead have been found in ores, it does not ordinarily occur in nature in the native state. It is the heaviest of all the base metals, having a specific gravity of 11.37. The color of the pure metal is bluish gray. The tensile strength is low — from 2600 to 3300 pounds per square inch. The pure metal is very malleable and can be rolled into sheets or hammered into foil, but it has not sufficient ductility to be drawn into wire. Lead melts at 327.4° C. and boils at 1525° C. Lead is so soft, especially when it is allowed to cool slowly, that the pure metal can be scratched with the thumb nail.

277. Chemical properties. If lead is melted in contact with air, it oxidizes quickly to PbO. It undergoes no change at atmospheric temperature in perfectly dry air. The best solvent is HNO_3, while HCl and H_2SO_4 have little or no action.

278. Economic situation. The United States is the largest consumer of lead in the world and normally produces about 40 per cent of the world's supply. Almost no metallic lead is imported into this country, although considerable base bullion comes in under bond for refining. Considerable lead ore, particu-

larly from Mexico and South America, comes in under bond for both reduction and refining. This smelting and refining is centralized in the hands of a few strong companies. The other important lead-producing countries are indicated in Table XXVI.

TABLE XXVI. LEAD PRODUCTION OF THE WORLD (IN METRIC TONS)*

	1910	1915	1918	1920	1923	1925	1926
Australia . .	105,897	102,721	169,415	6,113	124,042	150,263	151,886
Canada . .	14,967	21,009	23,314	24,198	50,456	115,209	128,265
Mexico . .	120,662	31,384	88,503	85,209	167,144	186,120	200,381
Spain . . .	190,523	171,472	169,709	175,195	127,514	138,200	147,392
United States	353,186	487,177	504,614	427,966	506,235	611,973	631,411
Belgium . .	40,715	16,770	20,630	16,040	51,100	66,300	61,762
Burma . . .	—	13,758	19,380	24,198	46,484	48,032	55,202
Germany . .	159,851	134,750	74,600	59,000	51,213	50,000	76,235

279. Marketing and prices. Lead is marketed in the form of bars, or pigs, weighing from 80 to 100 pounds, although for certain special purposes these may be made as small as 2 pounds. There are two marketing centers, New York and St. Louis. The price quoted in the former is usually from $2 to $5 higher than in the latter. Ordinarily this price is quoted on the basis of 100 pounds; that is, 6.90 Chicago means $6.90 per 100 pounds delivered in Chicago. More than 90 per cent of the domestic lead is consumed east of the Mississippi River, the consuming centers being Chicago, New York, Philadelphia, Boston, and St. Louis. The production of domestic lead is in the hands of about fifteen strong companies, so that the price is governed entirely by supply and demand. The price varies, more than anything else, with conditions in the automotive and paint industries. The fluctuation during recent years is indicated in Table XXVII.

TABLE XXVII. PRICE OF LEAD IN NEW YORK

	CENTS PER POUND		CENTS PER POUND
1911	4.420	1922	5.734
1915	4.673	1923	7.267
1918	7.413	1924	8.097
1919	5.759	1925	9.020
1920	7.957	1926	8.417
1921	4.545	1927	6.755

* Mineral Industry.

ORES OF LEAD

280. Ores. These may conveniently be divided into oxide and sulphide ores. While we have ores containing but one mineral of lead, such as galena and cerussite, these are uncommon. Ordinarily the lead ores contain, besides the gangue, various compounds of zinc, iron, and copper. The separation of these into products from which pure metals can be reduced is difficult, often impossible, in the present state of the metallurgical art. The average content of the ores now mined in the United States is about 5 per cent of Pb.

281. Galena. Galena (PbS) is the most common lead mineral. When pure it contains 86.6 per cent Pb. While it often occurs in the pure state, it is generally found more or less intimately mixed with sulphides of iron and zinc. Since galena has a high specific gravity (7.5), it can usually be separated by water concentration from other minerals. Galena almost always contains silver. Usually this amounts to but a few ounces per ton of ore, but some of the lead ores run as high as 2000 ounces of Ag per ton. Gold is also often present, but in much smaller quantities.

The melting point of galena ranges from 935° to 1120° C. When molten it is very fluid and penetrates into every crevice in the brickwork of a furnace. It is volatile below its melting point. With 100-mesh galena, ignition or oxidation begins at from 360° to 380° C.

282. Anglesite and cerussite. In general the oxide ores are not of much importance. While certainly desirable from a metallurgical point of view, since they can be easily reduced in the blast furnace without roasting, the large deposits have long since been exhausted, and today, in the United States, we are dependent upon the sulphide ores for the bulk of our lead.

Both anglesite ($PbSO_4$) and cerussite ($PbCO_3$) are found in nature. They are the result of the alteration of the original sulphide mineral by the oxygen of the air and by ground waters charged with CO_2, O, and various mineral salts. Ordinarily they are found close to the surface in the form of sandy or earthy residues mixed with sulphides, carbonates, and silicates of the other base metals. All gradations are encountered, from a piece of galena with only a film of oxide mineral on the surface to a solid piece of oxide mineral with a core of the original sulphide.

Both anglesite and cerussite are very friable and in crushing produce considerable fine material. Since these fine particles pass off with the tailings in gravity concentration, and are not amenable to flotation in the present state of the art, no attempt is made to concentrate them. If pure enough and of sufficient tonnage, they are reduced in an oxide blast furnace, but usually they are mixed with the roasted sulphide ore.

There are other lead minerals, as wulfenite ($PbMoO_4$), pyromorphite ($Pb_{10}Cl_2(PO_4)_6$), and vanadinite ($Pb_{10}Cl_2(VO_4)_6$), but none of these are considered commercial lead ores.

Table XXVIII gives analyses of some common lead ores:

TABLE XXVIII. ANALYSES OF LEAD ORES (IN PER CENTS)

	Pb	SiO_2	Fe	CaO	S	Zn	OUNCES OF Ag PER TON
Sulphide ore, Joplin, Mo.	5.7	5.0	4.1	25.5	2.0	—	0.12
Sulphide ore, Utah . . .	13.3	25.6	16.3	5.0	20.8	3.8	3.6
Oxide ore, Colorado . .	21.0	22.5	18.2	2.4	0.9	—	65.0
Oxide ore, Nevada . . .	33.2	3.0	24.1	1.1	2.0	—	27.5

283. Concentration. It is not profitable to smelt a low-grade lead ore. Smelters inflict high penalties on such ores, so that ordinarily it does not pay to smelt directly an ore with less than 35 per cent of Pb. Special conditions such as high precious-metal content or the presence of some desirable fluxing constituent may alter this. Low-grade ores can better be concentrated at the mine by some of the processes outlined under "Preparation of Ores," and the concentrates shipped to the smelter for treatment. Table XXIX shows the analyses of various types of lead concentrates and the degree of concentration.

TABLE XXIX. ANALYSES OF LEAD CONCENTRATES

	Pb	Cu	INSOLUBLE	Fe	CaO	Zn	S	Au	Ag
	Per Cent	*Per Cent*	*Per Cent*	*Per Cent*	*Per Cent*	*Per Cent*	*Per Cent*	*Oz. per T.*	*Oz. per T.*
Colorado	67.95	—	5.95	1.85	—	7.7	12.90	0.02	30.8
Colorado	38.85	1.0	1.6	11.8	—	14.05	7.4	0.08	21.9
Colorado	23.30	—	4.4	1.7	29.0	—	1.2	—	3.1
Idaho . .	63.1	—	2.0	4.0	—	8.3	15.4	—	26.5
Utah . .	32.0	Trace	30.0	2.1	4.6	7.2	3.2	—	4.2
Missouri	80.96	—	1.2	0.30	—	3.25	14.54	—	—

COMMERCIAL LEAD

284. Grades. Lead is one of the few metals which can be produced on a large scale in a very pure state. Lead containing over 99.8 per cent of Pb can be easily and cheaply made. Only at an exorbitant cost can we make iron, zinc, or nickel of such a high degree of purity. Lead appears on the market in the following grades: *soft lead,* made from very pure ores and containing very little silver or other impurity; *desilverized lead,* which is made from argentiferous, often very impure, ores, and purified by means of the Parkes or the Betts electrolytic process; and *antimonial,* or *hard, lead,* which contains from 15 to 30 per cent of Sb. Table XXX gives the analyses of some of the common grades of lead.

TABLE XXX. CHEMICAL ANALYSES OF COMMERCIAL LEAD (IN PER CENTS)

	SOUTHWEST MISSOURI	DESILVERIZED LEAD	ANTIMONIAL LEAD
Cu	0.0190	0.0006	1.861
Ag	0.0005	0.0004	0.004
Bi	Trace	0.0672	—
As	Trace	0.0010	—
Sb	0.0020	0.0062	12.753
Ni and Co	0.0018	—	—
Fe	0.0015	—	Trace
Zn	Trace	—	Trace
Pb (by diff.)	99.9752	99.9246	85.382

285. Uses. Desilverized and soft lead are used in the manufacture of sheet, pipe, shot, and various alloys of lead, and in the chemical industry for the production of litharge, red lead, and lead salts. The electrolytic grade is used in the manufacture of white lead (basic carbonate) for use as a paint. Antimonial lead is used for the making of type metal, bearing metals, storage-battery plates, and industrial alloys. Table XXXI shows other important uses of lead.

286. Effects of impurities. The amount of impurities found in commercial lead today is usually very small. For many industrial uses, however, the metal must be very pure. For example, lead which is to be corroded into white lead may contain only a very small amount of certain impurities if the product is to

TABLE XXXI. LEAD CONSUMPTION IN THE UNITED STATES (IN TONS OF TWO THOUSAND POUNDS)

White lead	130,000
Red lead and litharge	46,000
Storage batteries	143,000
Cable-covering	131,000
Building	75,000
Automobiles	7,500
Locomotives	2,100
Railway cars	6,000
Shipbuilding	100
Ammunition	39,000
Terne plate	4,600
Foil	28,000
Bearing metals	28,000
Solder	30,000
Type metal	12,000
Calking	25,000
Casting	15,000
Total	722,300

conform to commercial specifications. Lead which is to come in contact with acid solutions or is to be mechanically worked must be very pure. Of the common impurities Cu, Ag, Au, Bi, Cd, Sn, Sb, As, Fe, and Zn only the following ones are of much importance to the average consumer.

As little as 1 ounce of Ag per ton of lead gives the resulting white lead a decided reddish tinge and renders it unsuitable for the highest grade of paints. Such proportions, however, do not detract from the physical properties of the metal.

For corroding lead the limit of Bi is 0.05 per cent, since it gives a grayish tinge to the white lead. Lead is noticeably hardened by from 0.1 to 0.4 per cent of Bi. Lead with as much as 1.5 per cent Bi, however, can be rolled and worked as easily as soft lead.

The amount of As ordinarily found in lead does not detract from its desirable physical properties. The only industrial alloy of importance containing considerable quantities of this element is shot or shrapnel, which may run as high as 0.6 per cent As. Such alloys are hard and rather brittle.

Small quantities of Sb give lead a grayish-white color and make it harder and less malleable than ordinary lead. Corroding lead should contain not more than 0.005 per cent.

Zinc makes lead hard and brittle, so that it cannot be rolled or worked. Corroding lead should contain less than 0.0015 per cent.

287. Alloys. Although lead alloys readily with most metals, the alloys of lead in common use are not numerous. From an industrial standpoint, however, they are very important. The common alloys are as follows:

	Pb	Sb	Sn
Type metal	*Per Cent*	*Per Cent*	*Per Cent*
Best	50	25	25
Common	60	30	10
Linotype metal	85	12	3
Shrapnel	94	6	—
Pewter	20	80	—
Bearing metal			
Thin linings	95	4	1
Thick linings	86	11	3
Solder			
Half-and-half	50	—	50
Plumbers'	66	—	34

Lead is sometimes used in brass to soften it and make it machine easily. Calcium, barium, and the alkaline-earth metals are sometimes used for certain kinds of hard lead.

EXTRACTION OF LEAD FROM ITS ORES

288. Methods of reduction. Lead is almost universally extracted from its ores by pyrometallurgical methods. The ore is first roasted in order to oxidize and volatilize the sulphur and some of the impurities. The oxides and sulphates thus formed are then reduced, in a reverberatory furnace, ore hearth, or blast furnace, to metallic lead. The blast furnace is most common. In it, with a charge consisting of roasted ore, coke, and the proper fluxes, we produce (1) a bullion, which, if the ore was impure, must be softened and refined; (2) a matte or speiss, containing the sulphides and arsenides of the base metals; and (3) a slag, usually containing so little lead and precious metals that it can be discarded. Methods involving leaching and complete volatilization are now engaging the at-

tention of our metallurgists. Some of these methods have undoubted merit, but so far none have been successful enough to warrant their employment on a large scale.

THE ORE HEARTH

289. General. This, the oldest method of treating lead ores, has seen many ups and downs. Originally it was the only method of treating high-grade ores. The introduction of the blast furnace, however, with its high capacity, ability to treat impure ores, and many other advantages, caused most of the ore-hearth plants to close down. In 1914 about 75 ore-hearth plants were in operation in the United States, treating 230,000 tons of concentrates annually. These were gradually closed down until the development, a few years ago, of mechanical rabbling in the Newnam furnace. Today an increasing tonnage of pure ores is being reduced by this process. For such pure ores it is cheap and produces quickly a good grade of soft lead without expensive softening and refining.

To be suitable for reduction in ore hearths an ore must have the following characteristics:

1. The ore or concentrate must contain at least 55 per cent of Pb.

2. It must contain not more than 5 per cent of SiO_2, since this forms a silicate with the lead and is not reduced in the ore hearth.

3. It must contain not more than 10 per cent of iron pyrite or blende.

4. Sb, As, and Ag should be absent. The first two give an impure lead, and the latter cannot be recovered in the ore hearth.

290. Ore hearth. The common type of hand-rabbled ore hearth is shown in Fig. 95. It consists of a cast-iron well, or hearth box, set in the brickwork of the furnace. This well is about 2 feet long, $2\frac{1}{2}$ feet wide, and 1 foot deep, and holds about 2 tons of molten lead. In the front of the furnace is a "work stone" of cast iron. This slopes gently into the kettle where the lead is collected. The brickwork of the furnace is covered, sides and back, with heavy cast-iron plates. The rear one is perforated, as shown, for the introduction through the tuyères of

air under pressure. The hood and flue carry off the fume and dust, part of this settling out in a "blind flue," or pit, the rest being caught by a bag house or Cottrell apparatus. On the side of the shaft is a feed door for the introduction of fuel, the charge being fed from the front of the furnace. The front of the furnace may be closed by means of a sliding door. Such a furnace can be worked for only about fifteen hours, when the cast-iron

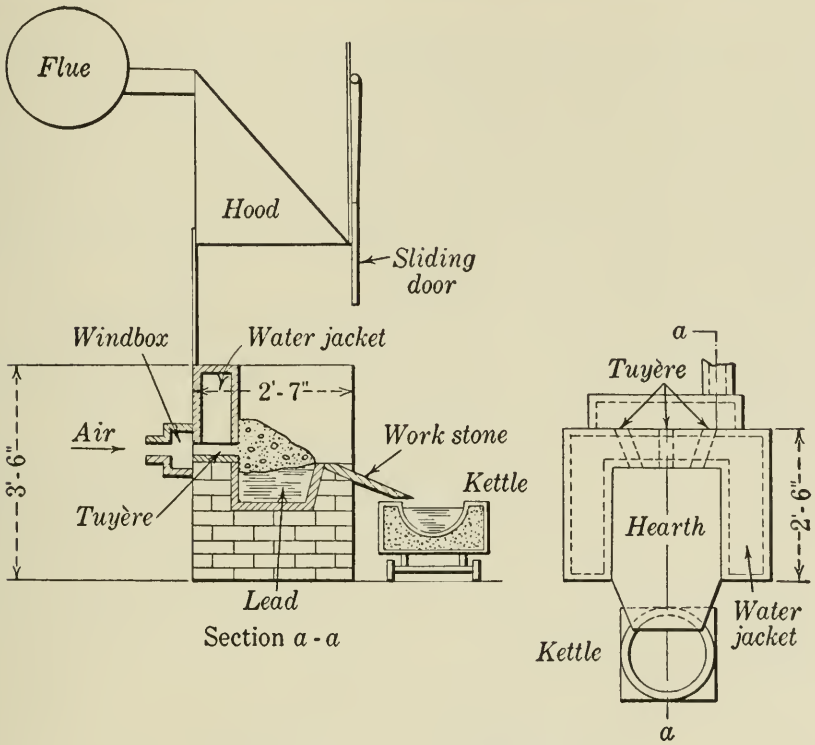


FIG. 95. An ore hearth

plates become too hot. Most American furnaces are built with water jackets in order that they may be operated continuously.

291. Operation. Let us assume that the hearth is in operation, with the well full of molten lead and a hot mass of coke, flux, and partly decomposed ore floating on the surface. To this mass is added from 15 to 30 pounds of ore mixed with from $1\frac{1}{2}$ to 2 per cent of lime, and covered with a little fuel. The blast is then turned on for from three to five minutes. The half-fused mass is then drawn out on the work stone. Two operators are required for a hearth. One man with a bar loosens the fused mass and stirs the charge; the other with a shovel or rake draws out the half-fused mass on the work stone, where the slag is

separated from the rest of the material. Molten lead also separates out and trickles down the grooves of the work stone into the kettle. Some lead is reduced in the furnace, collects in the well, and overflows through these same grooves. Slag as it is separated from the unreduced ore is thrown aside and lime is mixed with the undecomposed ore and put back into the furnace with a little raw ore, flux, and fuel, and the whole process is repeated.

The ore hearth is not suitable for argentiferous ores, since a good deal of lead and silver are volatilized. The gray slag produced contains a considerable amount of lead and must be retreated in a lead blast furnace. The recovery used to be as low as from 65 to 75 per cent of the lead content, but improvements, particularly in the Newnam hearth, have brought this up to over 85 per cent with pure ores.

292. Chemistry. The chemistry of the process is simple. The raw ore of the charge is heated by the fuel and oxidized by the air of the blast to PbO and $PbSO_4$:

$$2\ PbS + 7\ O = PbO + PbSO_4 + SO_2 \text{ (slow roast)},$$
$$3\ PbS + 10\ O = 2\ PbO + PbSO_4 + 2\ SO_2 \text{ (quick roast)}.$$

Only a part of the raw ore is thus oxidized in the three to five minutes of blast. The remainder reacts with the lead oxide and sulphate as follows:

$$PbS + 2\ PbO = 3\ Pb + SO_2,$$
$$PbS + PbSO_4 = 2\ Pb + 2\ SO_2.$$

The lime unites with the SiO_2 of the ore to form a fusible silicate. Any pyrite which is in the ore will be oxidized, and the FeO thus produced will enter the slag. There is some loss of lead through the formation of a lead silicate which is not reduced under the conditions prevailing in the hearth. This loss is high if the ore contains more than about 5 per cent SiO_2. Some of the PbO is probably reduced by C or CO.

293. The Newnam hearth. The chief objection to the old ore hearth was the high cost of labor. In the Newnam mechanically raked hearth, illustrated in Fig. 96, this difficulty is to a certain degree overcome, and since 1914 an increasing number of these hearths have been put in operation. They are particularly suited to the pure ores of the Mississippi Valley. The

hearth itself is similar in construction to the one already described. In front of the furnace, mounted upon an overhead track, is the mechanical rabbling machine. It has a mechanically operated rabble, or poker, which, as the truck moves down the furnace, plows its way through the crust of half-decomposed ore floating on the lead. This serves to stir this crust and break it up thoroughly, so that the operator can remove the slag. The hearth is 8 feet in length and longer than the hand-raked furnaces. The operator follows the machine with a rake or hoe, removes the slag which has formed, returns the undecomposed ore to the furnace, and adds raw ore, fuel, and flux as needed.

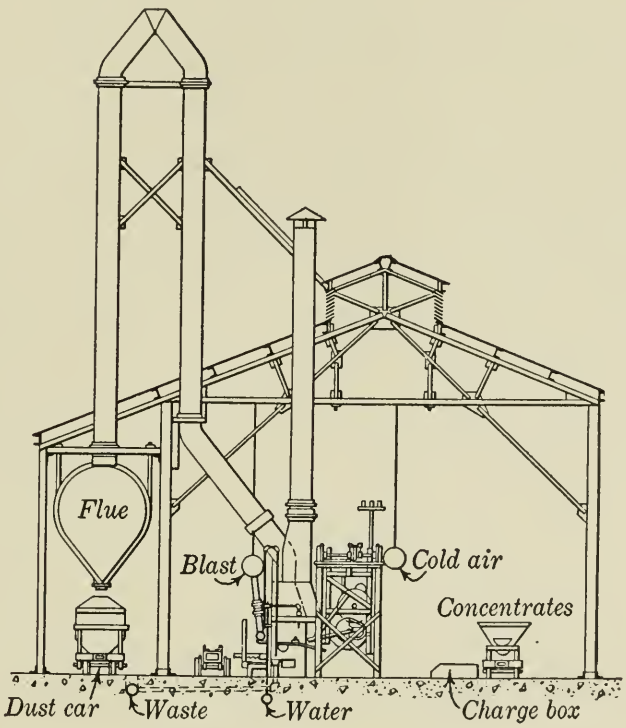


FIG. 96. The Newnam hearth

Where the tonnage to be handled is small and the ore or concentrate high-grade and free from silver or impurities, the elasticity and cheapness of the hearth-smelting operation has much to recommend it. Where it is impossible to sell this gray slag advantageously, it may be accumulated and periodically smelted in a small lead blast furnace. This slag is admirably adapted, both physically and chemically, to the blast furnace and ordinarily commands a ready market.

BLAST-FURNACE SMELTING

294. General. By far the greater portion of our domestic lead ores is reduced in the blast furnace. Sulphide ores containing more than 5 per cent of SiO_2, and all impure ores, must be so treated. Oxidized ores can be smelted directly, but sulphide

ores must first be roasted in order to remove the sulphur. The blast furnace, to be described later, is similar in principle to the copper blast furnace. The roasted ore, or oxide ore, with suitable proportions of fuel and fluxes, is charged into the blast furnace. Air admitted through the tuyères burns the fuel and furnishes the heat for the process. The lead sulphide reacts with the lead oxide and sulphate to produce metallic lead. Lead oxide is also reduced by the C and CO of the fuel. If the ore contains gangue in the shape of oxides and silicates of Fe, Ca, and Al, these unite with the SiO_2 of the charge to form a fusible slag which will not dissolve metallic lead. If there is any S present, it will form a matte with the Cu, Fe, Zn, and other base metals. These three — the lead, slag, and matte — are of different specific gravities, are not soluble in each other, and are easily separated. The precious metals which are present enter both the lead and the matte and are recovered later in the refining process.

295. Roasting of lead ores. Since all sulphide ores must be roasted, and since most of our lead today is derived from such ores, we will discuss first the principles of the roasting of these ores. From certain favored districts we still obtain pure ores which consist only of galena (PbS) and gangue (silicates and carbonates of Ca, Fe, Al, Mg, etc.), but by far the larger percentage of our concentrates is derived from complex ores. Such concentrates contain ordinarily, besides the galena and gangue, sulphides of zinc, iron, copper, antimony, and arsenic. The chemistry of the roasting process is a relatively simple one involving the following reactions:

$$2\,PbS + 7\,O = PbO + PbSO_4 + SO_2 \text{ (slow roast).}$$
$$3\,PbS + 10\,O = 2\,PbO + PbSO_4 + 2\,SO_2 \text{ (quick roast).}$$
$$FeS_2 + \text{heat} = FeS + S.$$
$$FeS + 3\,O = FeO + SO_2.$$
$$Cu_2S + 3\,O = Cu_2O + SO_2.$$
$$2\,ZnS + 7\,O = ZnO + ZnSO_4 + SO_2.$$

The roasting of galena must be carried out very carefully. Recent research has shown that if a roast is carried out at a temperature below 450° C., there is formed mainly $PbSO_4$. With slow oxidation and the presence of some catalyst all the PbS may be converted into $PbSO_4$. On the other hand, the more

the temperature rises above 450° C. the greater will be the amount of PbO formed. This is desirable for blast-furnace work, but there is a definite limit to the amount the temperature may be raised. If it is raised above 750° C., the galena will become pasty and agglomerate, and will retard the roasting. Reactions between PbS, $PbSO_4$, and PbO will set in to liberate lead which may be lost through oxidation. The proportion of PbO and $PbSO_4$ formed will therefore be dependent on the temperature, the admission of air, and the character of the minerals associated with the galena.

The metallurgist is always faced with the question of whether it is better to roast the ore or to smelt it directly. The character and the amount of the sulphides, the cost of roasting, and the richness of the ore will be the deciding factors. As a general rule, any impure ore containing over 8 per cent of S is best roasted before smelting. With ores rich in silver there is a heavy loss of Ag through volatilization, so that it is better to smelt some of these rich ores raw. The best way to do this is by adding them in small quantities to the ordinary ores. In this connection it may be stated that a lead ore with 100 ounces of Ag per ton, or more, is seldom roasted.

296. Roasting furnaces. These have already been described in detail in the chapter on roasting. Lead ores begin to give off their sulphur at a low temperature, so they may be roasted by any of the methods described; but today practice has been pretty well standardized in the use of the Wedge and Dwight-Lloyd furnaces. The sulphide ore is crushed to about 8 mesh and rough-roasted in a Wedge multiple-hearth furnace. This calcine is then given a finishing roast in a Dwight-Lloyd straight-line machine. This furnace can be adjusted to leave enough S in the ore to take care of the copper, and has the advantage of delivering a peculiarly sintered product much better adapted to blast-furnace work than to any other kind of machine, thus cutting down the loss by volatilization and being cheaper in cost of plant and of treatment.

297. Bedding lead ores. In all customs plants it is the universal practice to bed the ores, and even in smelters handling their own ores it is found advantageous to do this. The reason for it is apparent. Ores are received at the smelter in lots ranging from two or three tons to several carloads. These ores differ in

the amount of lead which they contain, in the character and amount of the impurities, and in their physical condition. Were these ores to be smelted one by one, it would mean that furnace conditions would be constantly changing — so much so that it is doubtful if the operator could keep the furnace in proper condition and at the same time recover the maximum percentage of lead and precious metals. By mixing all these small shipments together in a bed holding several hundred tons, it is possible to consider the mixture as a single ore and smelt it as such. By sampling, weighing, and assaying all the separate shipments the superintendent can calculate the composition of the whole bed and figure the fuel and fluxes for a campaign of several days or weeks instead of only a few hours. In making a bed of this sort, which may be from 3 to 10 feet deep, an effort is made to spread each ore over the entire surface of the bed in a thin layer. Then a vertical section taken at any point will be of the same physical character and chemical composition. Small amounts of ore, termed *side ores*, are kept on hand for varying the character of the charge at will, for fluxing purposes, etc.

298. Lead blast furnace. This differs only in minor details from the copper blast furnace already described. A 44×180 inch furnace is illustrated in Figs. 97A and 97B on pages 220, 221. In the copper blast furnace the crucible is shallow, relatively small amounts of melted materials accumulate in it, and as a rule no separation of slag and matte takes place in the furnace. In the lead blast furnace the crucible is deep and is tapped continuously by means of a lead well, or Arents siphon tap. This consists, as shown in the sectional elevation, of a channel of rectangular cross section connecting the bottom of the crucible and a small well outside the furnace. Lead, as it is reduced in the furnace, collects in the crucible, beneath the slag, and, by the pressure of this slag and the charge, overflows from the well. The slag is tapped off at intervals, so as to prevent its entering the tuyères, by a spout indicated on the left of the side elevation. This spout is high enough above the surface of the lead in the crucible to prevent any lead from being sucked out with the slag. The furnace is water-jacketed on all sides from just below the level of the tuyères up to the charging floor. There are from four to eight separate jackets to facilitate repairs. Each jacket has an individual feed pipe for supplying cooling water.

The working height of the furnace varies from 16 to 24 feet. The horizontal cross section varies from 40 × 144 inches up to 60 × 180 inches. Furnaces smaller than 40 × 120 inches are usually made circular in cross section. Lead blast furnaces are never made in as large units as copper blast furnaces (81 feet in length at Anaconda) for two reasons: (1) The process of lead smelting is a delicate one; it is difficult enough to keep a furnace 44 × 180 inches in operation, and it would be impossible to keep a furnace two or three times that length in satisfactory condition. (2) The tonnage of ore handled, owing to the fact that it is of much higher grade, is very much smaller than that of copper, and large furnaces would work at less than their capacity most of the time and consequently would be inefficient.

The issuing gases from a lead blast furnace have no fuel or chemical value; so these furnaces are run with an open top. They may be temporarily closed with sliding doors, as indicated in the illustration.

The diameter of the tuyère opening is from $3\frac{1}{2}$ inches to $4\frac{1}{2}$ inches, and the distance between centers is from 16 inches to 18 inches. There are no tuyère openings in the ends of the furnaces, but only on the sides. The air is supplied at a pressure of from 28 to 50 ounces per square inch and is never preheated as in the iron blast furnace. The apparatus for furnishing the blast is usually of either the Roots or the high-speed-turbo type.

The water jackets may or may not be covered with brickwork. Of course this helps to conserve the heat, but it makes repairs to the water jackets a little more difficult. The mouth of the furnace is connected with the main flue by means of a gooseneck for the withdrawal of the fume and the products of combustion.

299. Blowing-in a blast furnace. The crucible is first warmed, by means of a light wood fire, for about twenty-four hours in order to drive off the moisture. When this is done properly, the crucible will be warm to the hand on the outside. It is then cleaned out and filled, up to the tuyère level, with pigs of lead piled crosswise in order that the heat may penetrate the pile more easily. A 46 × 162 inch furnace will require about 50,000 pounds of lead. Light kindling and oil-soaked waste are placed in front of the tuyère openings and cordwood charged to a depth of about 3 feet. On top of the wood are placed the blowing-in charges, which consist of coke and old slag. The

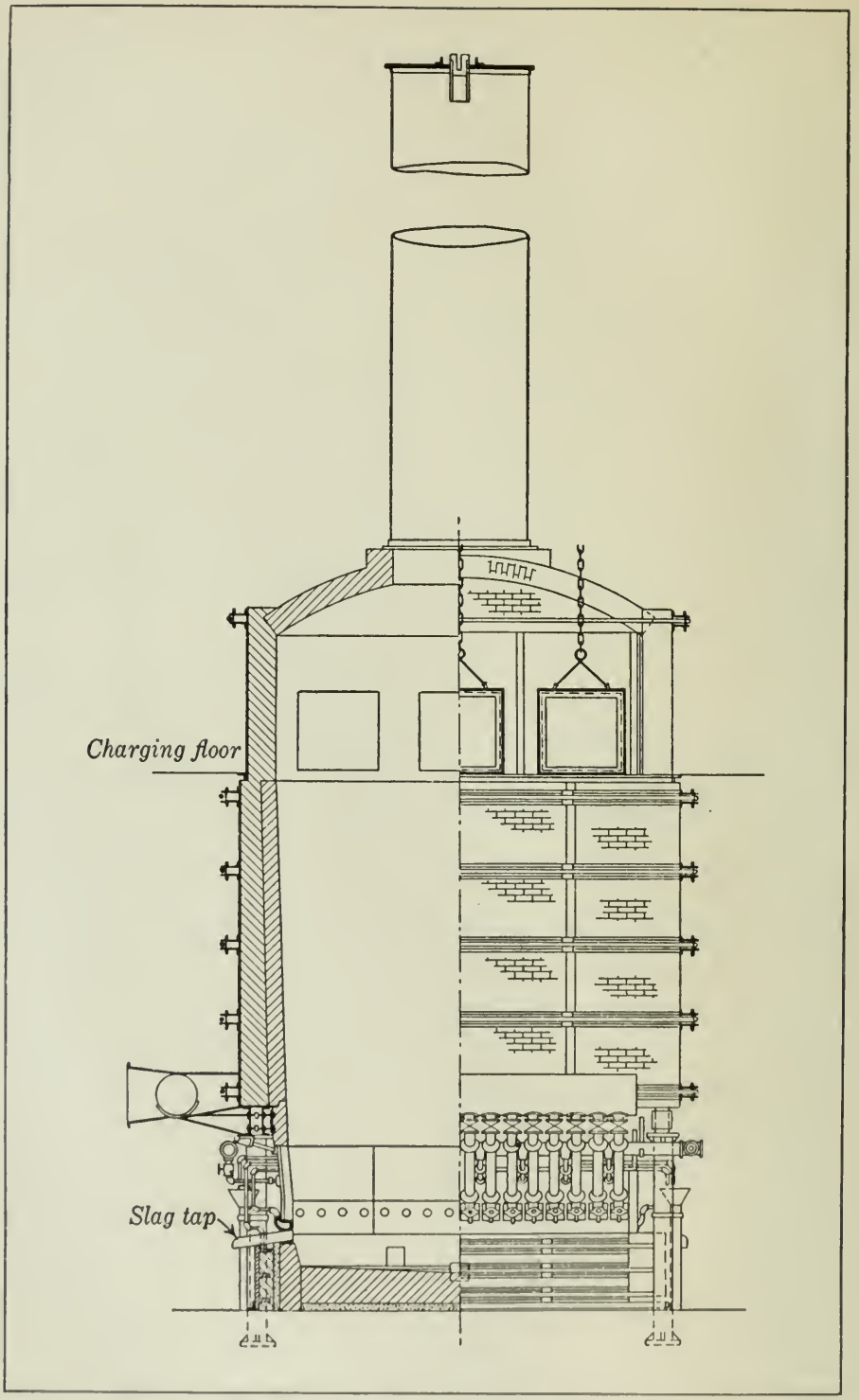


FIG. 97A. The lead blast furnace (side elevation)

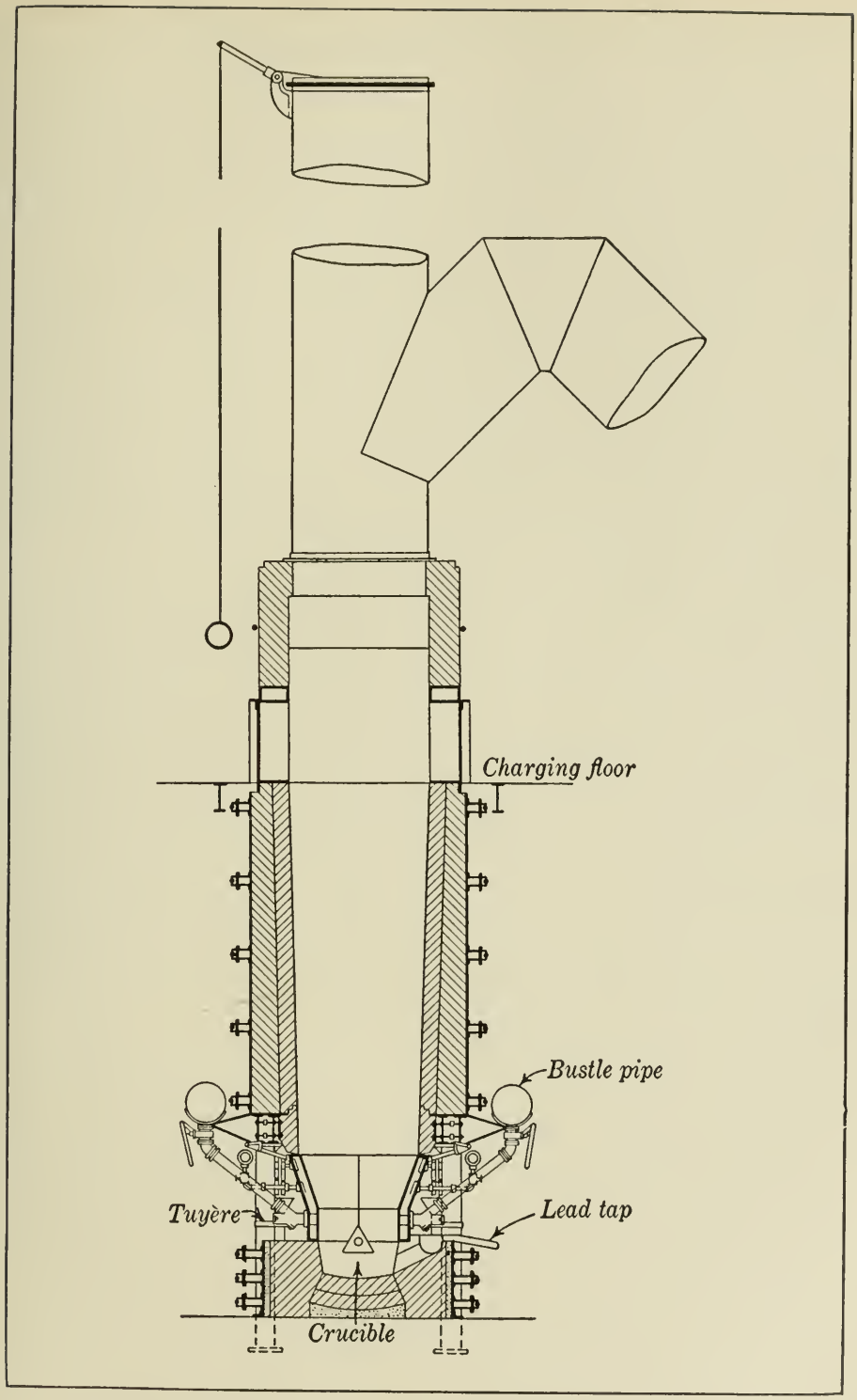


FIG. 97B. The lead blast furnace (sectional end elevation)

furnace is then lighted, and after about ten minutes a light blast is turned into the tuyères. At the end of about two hours the crucible is full of molten lead, and the first slag is drawn off at the slag tap. Increasing amounts of ore are added to the blowing-in charges, and the blast pressure is increased little by little, until at the end of about seven hours the normal working charge is reached.

300. Operation of the furnace. Fluxes and fuel are stored in hopper-shaped bins, from which they can easily be drawn as needed. In small smelters ore from the bedding plant, fuel, and flux are weighed into small barrows or buggies, wheeled to the furnace by hand, and dumped onto the feed plate in front of the furnace, and the charge is fed in by hand as required. It is essential that this weighing be carefully done, or the operator cannot possibly produce the proper slag.

Several methods of mechanical charging are in use at the larger smelters. In all these the cars are brought over the top of the furnace (the charge being kept at a level from 3 to 4 feet below the charge floor), and the contents of the car are dumped through a movable door into the furnace. The methods of distributing the charge vary. At some plants each car consists of a properly proportioned charge; at others one car contains ore, the next flux, and the next coke. Even distribution, however, is essential in order that the gas current may rise evenly and no dead spots form in the furnace. In general, this distribution should be such that the coarse ore is at the middle of the furnace and the fine ore at the walls and corners.

In tapping slag the furnace-operator knocks out the fire-clay plug which closes the tap hole and allows the slag, matte, and speiss to flow into a settler, where the matte and speiss collect. The slag overflows into a slag car to be taken to the dump, or it may be granulated with water. In tapping, it is general practice always to keep some slag in the furnace. The lead is tapped from the well into a large pot in front of the furnace, drossed, and cast, either by hand or by machine, into pig form. The amount of lead withdrawn at one tapping is limited to about 1500 pounds in order not to empty the crucible completely. The dross from the lead is returned to the furnace to be resmelted.

The operation of a lead blast furnace is much more delicate than that of a copper blast furnace. Both lead and silver, under

certain conditions, volatilize easily; hence the furnace must be run with a cold top, — that is, show no visible heat or flame (overfire). The best remedy for overfire is to reduce the percentage of coke or else allow the charge level in the furnace to sink slowly and then fill the furnace with 2 or 3 feet of cold charge. Wall accretions form on the ends and sides of the furnace shaft and are an endless source of difficulty, holding back the charge and cutting down the capacity of the furnace. They are caused by excessive amounts of unroasted galena, sphalerite, and compounds of As and Sb in the ore. They begin to collect just above the water jackets and sometimes reach to the charge floor. In mild cases "barring down" with a heavy steel bar may dislodge the accretions, but often the furnace-operator may be obliged to close down and empty the furnace. Hearth accretions are another source of trouble. They form in the shape of a crust over the top of the crucible and prevent reduced lead from dropping into it. The only way to remove them and still keep the furnace in blast is to break the crust with a heavy bar or punch holes in it and allow the hot lead and slag to pass through and melt it down.

301. Products of the blast furnace. The products of the lead blast furnace are lead bullion, matte, wall accretions, hearth accretions, flue dust, slag, and gas.

302. Bullion. Lead bullion from the ores of the Mississippi Valley is termed soft lead, since it is pure enough for most commercial uses. As indicated by the analyses in Table XXXII on page 224, most lead bullion must be softened or desilverized before it is pure enough to be used in industry. It is cast into bars about 3 feet long, 4 inches wide, and 3 inches deep, weighing from 80 to 110 pounds. This bullion contains, besides the lead, silver, and gold, a varying percentage of impurities such as Cu, Fe, Zn, As, and Sb. The Au and Ag, if small in amount, can be left in lead which is to be used for other purposes than the manufacture of white lead. The other impurities detract from the physical and chemical properties of the metal and must be removed by softening. If there is enough Au and Ag to warrant it, these metals may be recovered by the Parkes process or the Betts process. The lead content of the bullion may fall as low as 90 per cent in smelting ores which contain stibnite or other antimony compounds.

TABLE XXXII. ANALYSES OF LEAD BULLION

	LEADVILLE, COLORADO	TRAIL, BRITISH COLUMBIA
	Per Cent	*Per Cent*
Pb	98.4924	98.860
Ag	0.7934	0.412
Bi	0.0118	0.0013
Cu	0.0715	0.05
Cd	Trace	Trace
As	Trace	0.28
Sb	0.3479	0.35
Fe	0.0126	0.01
Zn	0.0002	Trace

303. Speiss. The predominant element in arsenical speiss is Fe. The other metals are Co, Cu, Pb, Bi, Au, and Ag. An antimonial speiss is seldom produced, since the Sb is usually reduced and enters the bullion. The treatment of speiss is difficult. Very often it is treated in conjunction with the matte, although this is admittedly a poor method. Roasting and resmelting is an expensive method but about the only satisfactory one.

304. Matte. The matte produced in the lead blast furnace usually contains from 45 to 60 per cent of Fe, from 10 to 15 per cent of Pb, from 5 to 10 per cent of Cu, and from 22 to 25 per cent of S. Except for the high lead content it is much the same as the low-grade mattes produced in the copper blast furnace. A "leady" matte is first roasted to eliminate the S and to oxidize the Fe. This calcine is then smelted with the proper fluxes in a small blast furnace to produce metallic lead, which carries most of the Au and Ag and a rich Cu-Fe matte which can be sold to a copper smelter, where it will be blown to metallic copper in a converter.

305. Slag. Lead slags, as indicated in Table XXXIII, show a wide variation in composition. This is due to the complexity of the lead ores now being treated. A lead slag should normally contain not more than 0.7 per cent of Pb and 0.5 ounces of Ag per ton. The specific gravity should not be higher than 3.6; if it is, there is an imperfect separation of matte and slag.

The slags are termed quarter, half, or one-to-one, depending upon the ratio of CaO to FeO. The kind of slag used will depend

upon the character of the ore and the kind of fluxes available. If the ore is siliceous, the operator endeavors to use a siliceous slag with as little outside flux as possible. On the other hand, if small amounts of ores high in CaO and FeO were available, he might be able to produce a more basic slag at a slightly increased cost. Slags may be admittedly "dirty," the superintendent may know that they can be improved, and yet fluxes may be so expensive as to render the recovery of a few more pounds of lead per ton unprofitable. Probably the most satisfactory, and hence the most common, lead slag is the three-quarter slag. This is particularly true at customs smelters, where a wide variety of ores allows the operator a wider choice in the matter of slags. Furnace and hearth accretions may be removed and general smelting conditions improved by altering for a short time the character of a slag.

TABLE XXXIII. COMPOSITION OF LEAD SLAGS (EXPRESSED IN PER CENTS)

TYPE	SiO_2	Fe(Mn)O	Ca(Ba, Mg)O
Quarter slag	28	50	12
Half slag	30	40	20
Three-quarter slag	33	33	23
Siliceous three-quarter slag	36	31	23
Whole, or one-to-one, slag	35	27	28

306. Flue dust. The flue dust, much larger in amount than that produced in the copper blast furnace, may contain as high as 60 per cent of Pb. Table XXXIV on page 226 gives typical analyses of this product.

This flue dust is very finely divided and can be recovered only by a bag house or by the Cottrell apparatus. It may be treated in several ways. Dampened, it may be fed into the same blast furnace. Of course, only a small part of it will be smelted; the rest returns to the flue-dust system, and eventually a large part finds its way up the stack into the atmosphere. A better way is to briquette the flue dust with milk of lime or some other binder. The briquettes formed can be fed immediately into the blast furnace, but it is better practice to air-dry them first.

A blast furnace 44 × 154 inches will require about 6500 cubic feet of air per minute and will produce over 8000 cubic feet of

gas. This escapes at a low temperature (150° C.), so that it is difficult to extract the heat from it economically. Since it is low in SO_2, it has no value as a source of sulphuric acid.

TABLE XXXIV. ANALYSES OF FLUE DUST (EXPRESSED IN PER CENTS)

	GLOBE SMELTER, DENVER	PUEBLO, COLORADO
Pb	—	25.60
PbO	37.65	—
Zn	—	4.74
ZnO	5.32	—
Cu	Trace	0.95
As	—	—
Sb	—	—
Ag	0.04	33.40 (ounces per ton)
Au	—	0.14 (ounce per ton)
Fe	12.05	13.40
CaO	5.26	5.30
Al_2O_3	1.31	—
SiO_2	8.63	26.20
S	2.53	4.20

307. The bag house. This is a device for removing the finest dust and fume from the gases produced in the smelting of copper, lead, and zinc ores, particularly the last two. Fig. 98 shows such a bag house in transverse section. It consists of a chamber 21 feet wide and 150 feet long. The whole chamber is subdivided into a number of smaller ones, so that while some are being cleaned of flue dust or being repaired the others may be in operation. The gas is freed of dust particles and fume by being passed through a number of cotton or woolen bags suspended in the chambers. These bags are about 12 inches in diameter and 34 feet long, tightly fitted over thimbles in the bottom of the chamber and suspended from 2-inch pipes at the top so that the gas must pass through the cloth in order to escape into the chimney flue. The gas, under slight pressure, is brought from the smelter in the flue *a*. Opposite each chamber is a damper to control the amount of gas entering that particular chamber. It is good practice to add a small amount of finely divided quicklime to the gas current in the chamber *a* in order to neutralize any H_2SO_4 which may have been formed, thus prolonging the life of the bags. The gas passes through the

interstices in the bag, leaving a deposit of flue dust, and escapes to the atmosphere or Cottrell apparatus through the flue *d*.

About every eight hours a chamber is cut off for cleaning. When the supply of gas is cut off, the bag collapses and most of the flue dust falls to the bottom of the chamber *b*. The bag

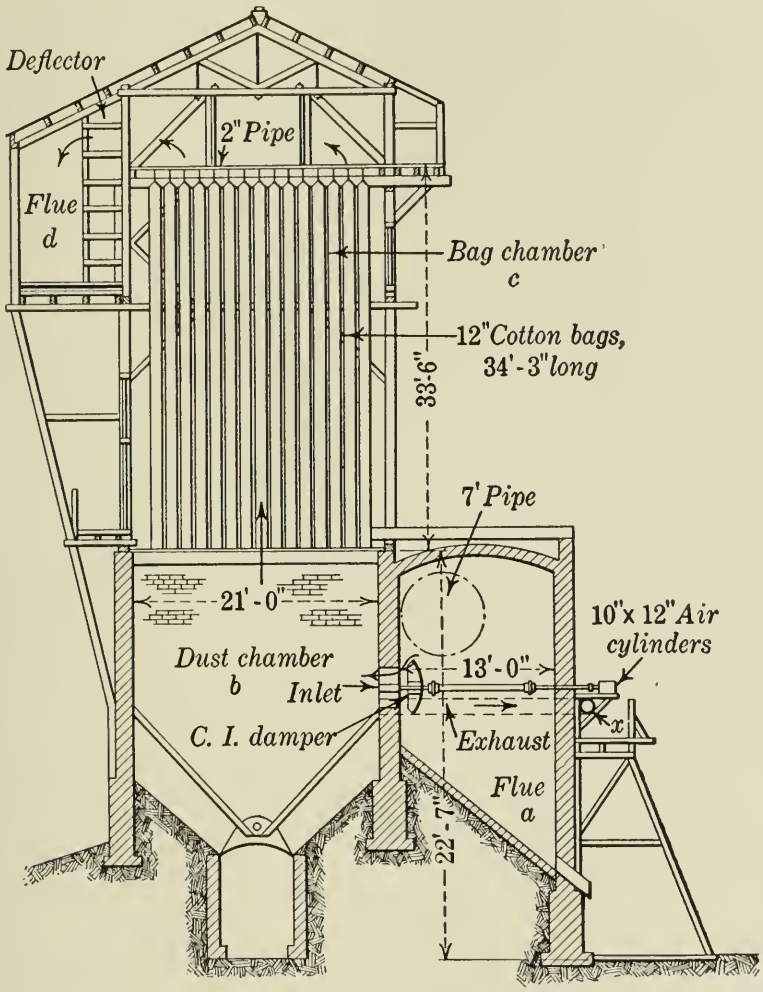


FIG. 98. The bag house

is shaken, either mechanically or by hand, to remove as much of the flue dust as possible. This dust collects in the hopper bottom and is removed by a helical screw into a car.

308. Chemistry of blast-furnace smelting. In a normal furnace the top of the charge is at a temperature of about 200° C. There the entrained moisture of the charge (normally about 5 per cent) is driven off. Some of the hydrates also lose their water of composition. Just below the surface of the charge,

reduction of ferric oxide by the rising gas current begins. The limestone is decomposed. These reactions increase as the charge descends until, at a point about halfway down the shaft, and at a temperature of 800° C., they are complete:

$$Fe_2O_3 + CO = 2\,FeO + CO_2.$$
$$CaCO_3 = CaO + CO_2.$$

Some PbO is reduced by the CO of the gas current, and reactions between $PbSO_4$, PbO, and PbS also set free Pb and SO_2. Galena may also react with iron oxide and carbon to set free lead:

$$PbO + CO = Pb + CO_2.$$
$$PbSO_4 + PbS = 2\,Pb + 2\,SO_2.$$
$$PbS + 2\,PbO = 3\,Pb + SO_2.$$
$$PbS + FeO + C = Pb + FeS + CO.$$

Scrap iron may be added to the charge in order to decompose any galena that may be left:

$$PbS + Fe = FeS + Pb.$$

Any Sb is reduced like the lead, and alloys with it. The molten lead trickles down through the charge and absorbs the gold and silver from the ore. Any lead sulphate not reduced by PbS may be reduced by iron oxide and carbon:

$$PbSO_4 + FeO + 5\,C = Pb + FeS + 5\,CO.$$

Copper has such a strong affinity for sulphur that copper sulphide is not reduced in the blast furnace. It unites with the iron sulphide of the charge to form a matte. This matte will also take up lead to the extent of from 10 to 20 per cent, and it is to cut down this loss that scrap iron is added. The matte dissolves a little of the gold and silver, but this is recovered when the matte is reduced. $CaSO_4$, $BaSO_4$, and $ZnSO_4$ will be reduced to their respective sulphides, and part of these will enter the slag.

The iron oxide unites with the SiO_2 of the charge to form a fusible ferrous silicate:

$$FeO + SiO_2 = FeSiO_3.$$

This in turn dissolves the oxides and silicates of Ca, Al, Mg, etc. to form the slag. If the fluxes have been correctly apportioned, the slag will dissolve only small amounts of lead and precious metals.

Any compounds of As which may be present are reduced to a speiss (Fe_4As) as follows:

$$As_2O_3 + 8\ FeO + 11\ C = 2\ Fe_4As + 11\ CO.$$

In the zone of fusion, below and just above the tuyères, at a temperature of from 900° to 1200° C., all the products are liquefied. Being of different specific gravities (lead 11.5, speiss 6.0, matte 5.2, and slag 3.6), they separate readily, in the crucible, into different layers. The lead is drawn out through the siphon tap. The slag, matte, and speiss are tapped off together, and final separation is effected in a slag pot outside the furnace.

309. Smelting of impure ores. A lead ore containing only siliceous or calcareous gangue and galena is relatively easy to smelt. Unfortunately such ores are scarce today, and we are dependent upon complex ores containing, besides lead, compounds of Zn, Mn, Ba, Ca, etc. Many of these cause difficulties and irregularities in smelting.

Usually a penalty is inflicted for more than a limited amount of zinc. Zinc tends to form a pasty, difficultly fusible slag from which the matte or metal is not easily separated. If present it goes into both the slag and the matte, increases the specific gravity of the former, and decreases the specific gravity of the latter, still further interfering with the completeness of separation. Zincky slags also promote the formation of both wall and hearth accretions.

Mn, aside from adding to the fusibility of the charge, acts in much the same way as iron and is figured as such in calculating a charge. Slags high in Ca are desirable, since they have a low specific gravity and lime is usually a cheap flux. High-Mg slags, on the other hand, tend to be pasty and streaky, somewhat like zincky slags. Dolomitic limestones as fluxes are therefore to be avoided if possible.

Copper should be avoided, but if it is present, by proper smelting most of it can be collected in the matte. If there is insufficient sulphur in the charge (and this is often the case in treating oxide ores), the copper is reduced and goes into the base bullion, making it so stiff and pasty as to interfere with its withdrawal through the lead well. Arsenic, if present in small amounts, is volatilized; if present in larger amounts, it unites with the iron to form a speiss.

310. Fuel. Either coke, charcoal, or a mixture of the two may be used as a fuel. The former, owing to its lower cost and greater strength, is almost universal. In this country a coke containing from 10 to 20 per cent of ash and from 75 to 90 per cent of fixed carbon is used. In calculating the charge this ash must be taken care of with the proper fluxes. The amount of fuel used will vary from 10 to 15 per cent of the charge, depending upon the nature of the ore being treated. It is never much lower than 10 per cent, for in lead smelting practically none of the S of the charge is available as fuel. In smelting the complex ores noted in the preceding paragraph it is often necessary to use a high percentage of coke in order to melt the pasty, viscous slags which form.

DESILVERIZATION OF BASE BULLION

311. General. Soft lead, which comes from very pure, non-argentiferous ores, may be purified sufficiently for ordinary market requirements by drossing. Most of our lead bullion, however, contains precious metals well worth recovering, or other impurities which detract from some of the valuable properties of the pure metal. Base bullion, as produced in most of the smelting centers of the United States, contains from 40 to 500 ounces of Ag per ton, from 0.1 to 2.0 ounces of Au per ton, and small amounts of Cu, Sb, As, Fe, S, and Zn. Refining is carried out by either the Pattinson or the Parkes process. In either case the bullion must first go through a softening process for the removal of the impurities other than Au and Ag.

312. Softening furnace. This consists of a water-jacketed reverberatory furnace, shown in Fig. 99. The hearth is 13 feet wide and 29 feet long and carries a bath of lead from 12 inches to 16 inches deep. In large plants furnaces holding as much as 350 tons are used. The water jacket keeps the refractory lining cool and prevents slagging by the PbO. The hearth and walls are constructed of high-grade fire brick. A variety high in Al_2O_3 gives the best service. At the slag line bauxite brick has been used. The base bullion is charged through the front doors, and the charge worked through the rear doors. After the softening process is completed, the molten lead may be removed

through the tap hole. The furnace is heated by fire box *f*, the products of combustion escaping through the flue *d*.

313. The softening process. The softening process is divided into two stages in order that the copper may be removed separately. In the first stage the lead, carefully piled, a bar at a time, on the hearth, is slowly melted down. Air is excluded until a state of quiet fusion has been reached. For about two hours the furnace is held at a temperature just above the melting point of the lead. During this period a dross, the "copper scum," rises to the top of the bath. By means of a perforated skimmer this is removed through the working doors. This dross contains most of the drossy lead, iron, and sulphur and nearly all the copper. This dross can be easily reduced, in a small blast furnace, to metallic lead and copper matte, and most of the valuable metals thus recovered. This dross will contain about 60 per cent Pb, 18 per cent Cu, and 2 per cent As, and will amount to from 3 to 7 per cent of the charge.

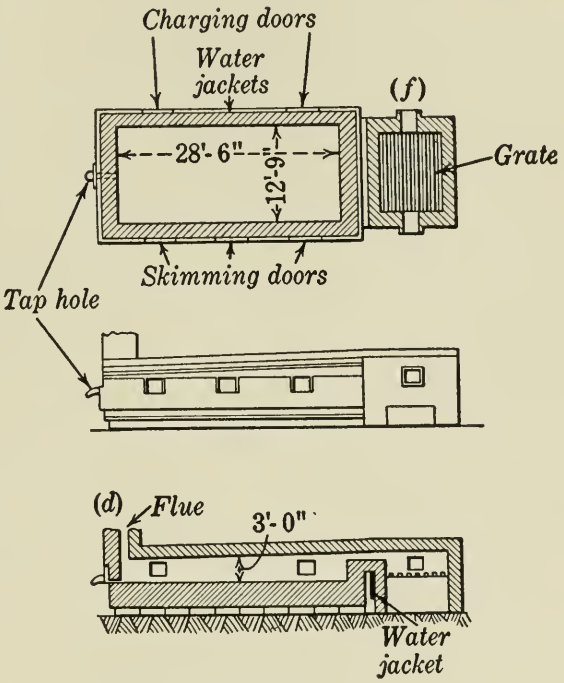


FIG. 99. A softening furnace

During the second period the temperature of the bath is raised to 600°–650° C., and air is freely admitted to the furnace, so that oxidizing conditions prevail. The lead is oxidized to PbO and the As and Sb to their respective oxides, which unite to form a litharge slag. This slag then serves to protect the lead from excessive oxidation. The bath is held at this temperature for about twelve hours, and during this time nearly all the As and Sb and the last of the Cu are removed. When, in the judgment of the operator, the softening is completed, the furnace is cooled slightly, and the dross (impure litharge containing from 15 to 20 per cent of Sb) is removed

with a perforated skimmer. This dross is smelted in a special blast furnace to hard, or antimonial, lead, which commands a ready sale. The lead remaining in the furnace contains now only Au and Ag, which are recovered by either the Parkes or the Pattinson process.

THE PATTINSON PROCESS

314. General. This process is based upon the fact that if lead containing small amounts of gold and silver is melted in a kettle and then slowly cooled to its freezing point, crystals of lead will separate out which contain less Ag than the original lead. These crystals may be removed to another kettle, more lead added to the first, and the process repeated. When the second kettle has been filled, it may be crystallized in a similar manner to produce a still lower grade of lead. By repeated crystallizations the base bullion may be separated into two products: a soft lead containing about 1.25 ounces of Ag per ton and a rich lead containing 450 ounces of Ag per ton. Theoretically the enrichment can be carried to 650 ounces of Ag per ton, but practically 450 ounces is found to be the limit. This enriched product must be cupeled to recover the Ag and Au. Owing to the fact that the rich lead constitutes such a large proportion of the original lead, the cost of cupellation is prohibitive and the Pattinson process is not commonly used today.

315. Operation. The process is carried out in a series of cast-iron kettles, each holding from 6 to 15 tons of lead. These kettles are set in brickwork and heated from a fire box below. When in operation, with, let us say, 15 kettles in the series, kettle No. 1 will contain lead with about 1.25 ounces of Ag per ton; No. 7, about 30 ounces of Ag per ton; and No. 15, about 450 ounces of Ag per ton. Intermediate kettles will contain lead of a corresponding tenor in silver. Bullion to be desilverized will be added to the kettle of the nearest silver tenor, let us say No. 7, and melted down. This kettle will be cooled very slowly, the crystals removed to kettle No. 6, and the liquid lead ladled out into kettle No. 8. More bullion will be charged into No. 7, and while this is melting down similar crystallizations will be carried out in the other kettles, the crystals moving toward No. 1 and the liquid lead toward No. 15. Soft lead with about 1.25 ounces of

Ag per ton will be removed from kettle No. 1, and rich lead for cupeling, from kettle No. 15. Dipping out the crystals by hand is a slow process; hence in large plants the kettles are so constructed that they may be raised mechanically over the next in line and the crystals removed by pouring the lead through a strainer. At best the cost of operation is higher than in the Parkes process, and the Pattinson process is seldom used today. The only advantage which the Pattinson process enjoys is that it removes the Bi. This follows the lead in the Parkes process. Bi is especially injurious in lead to be used in the manufacture of white lead, but today bismuth-bearing ores are seldom used to make lead for this purpose.

THE PARKES PROCESS

316. General. This process is based upon the fact that if lead bullion containing small amounts of gold and silver is melted down, and from 1 to 2 per cent of Zn is stirred into the charge, the Zn will form an alloy with the Au and Ag. This alloy is less fusible than the lead, of a lower specific gravity, and insoluble in Pb, which is saturated with Zn. The Zn-Ag-Au compound rises to the surface as a scum or dross and may be removed for further refining. By repeated zinckings the lead may be freed from most of the Au and Ag, and the precious metals may thus be concentrated in a product containing from 2000 to 4000 ounces of Ag per ton instead of 450 as in the Pattinson process. This reduces very materially the amount of rich lead which must be cupeled.

317. Softening. The bullion must be carefully softened in order to remove all the impurities other than Ag and Au. The details of this have already been discussed. The Parkes process is carried out in a cast-iron zincking kettle. Fig. 100 shows a cross section of a modern furnace for this purpose. This kettle is 5 feet 6 inches in depth by 11 feet in diameter. It would hold 100 tons of lead, but since 4 inches must be allowed for drossing purposes, it is rated as a 90-ton kettle. The weight of the furnace, lead, and stirrer (about 125 tons) is carried on steel columns set in the circular concrete wall *a*. These columns terminate in a heavy cast-iron ring which in turn supports the kettle. From the top of the concrete wall up to the cast-iron

ring the wall of the furnace is of brick, — common red brick outside, fire brick inside, with Sil-O-Cel brick in between as indicated. The space between the Sil-O-Cel and the concrete wall, as well as below the uptake, is filled with sand or granulated slag. The grate area is 2 feet by 4 feet 7 inches. It has been found that owing to the high efficiency of this type of construction, the furnace consumes no more coal in melting 90 tons of lead than the ordinary furnace consumes in melting 30 tons.

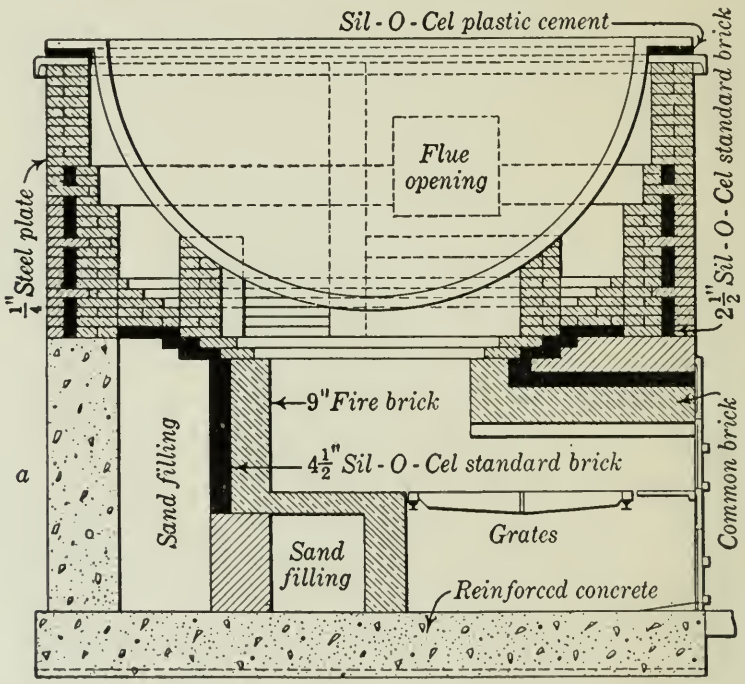


FIG. 100. A 90-ton lead kettle

318. Zincking. The kettle is filled with molten lead from the softening furnace. Slabs of metallic zinc, together with "floor zinc" from previous zinckings, are then added and allowed to melt, and the mixture is thoroughly stirred by means of a power-driven propeller (Howard stirrer), shown in Fig. 101. The machine consists of a cover *c* which fits tightly over the kettle. In the center of this is a propeller *b* mounted in a cylinder *a*. The cylinder is open at the top and bottom to allow a free flow of the molten lead. The machine is brought to the kettle by an overhead crane and lowered into it by means of chain blocks, and the propeller is started. The direction of rotation is such that lead will be drawn from the bottom of the kettle and will over-

flow the edge of the cylinder, which is about an inch above the surface of the lead in the kettle. After a few minutes the cylinder will be lowered a little and the direction of rotation reversed so that a thorough mixing is assured. The Zn combines with the Ag and Au to form an alloy of as yet uncertain composition. This alloy has a higher melting point and a lower specific gravity than pure lead. It is also insoluble in lead saturated with zinc. The kettle is then cooled slowly to a temperature between the melting points of pure lead and the Zn-Ag-Au alloy. The latter

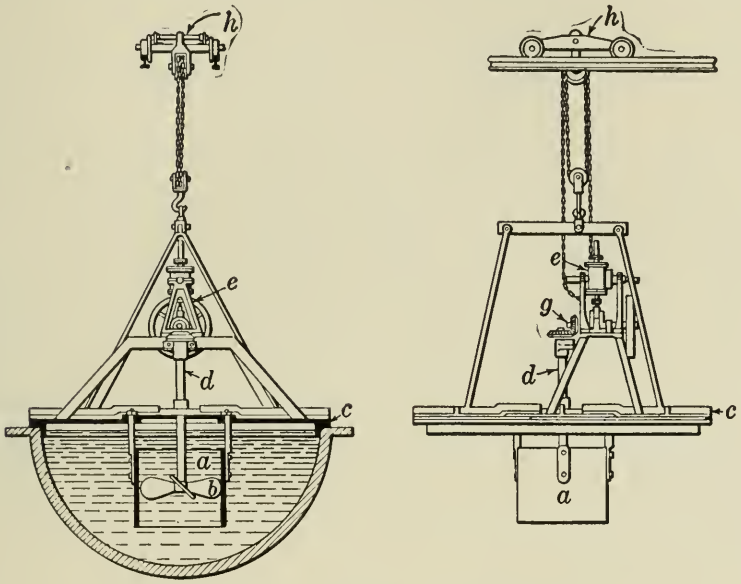


FIG. 101. The Howard stirrer

crystallizes out and rises to the surface as a dross, or crust. Ordinarily the drossing is carried out in a number of stages, the dross blocks from the second stage of each lot of bullion being used for the first stage of the succeeding lot. By this means the amount of low-grade crust is kept at a minimum.

The dross is removed by means of a Howard press, shown in Fig. 102. It consists of a cylinder *a* with a hinged bottom *b* and a plunger *c*. The whole apparatus is lowered into the kettle until the edge of the cylinder *a* is just a little above the surface of the molten lead in the kettle. By means of the hand wheel the plunger is raised out of the cylinder, and the crust is raked into it with a hoe or shovel. When the press has been filled with crust it is raised above the surface of the lead, the plunger is lowered, and considerable pressure is brought to bear on the crust. The

liquid lead is squeezed out and falls through the perforated bottom into the kettle below. When freed of the last of the lead the press is taken to one side, the hinged bottom is dropped, and the dry scum is allowed to fall out onto the floor. It is brittle when hot and can be readily broken up with hammers to a size convenient for charging into the retorts. This zincking process is repeated several times, until nearly all the silver has been removed. The lead remaining in the kettle will contain approximately 0.7 per cent of Zn.

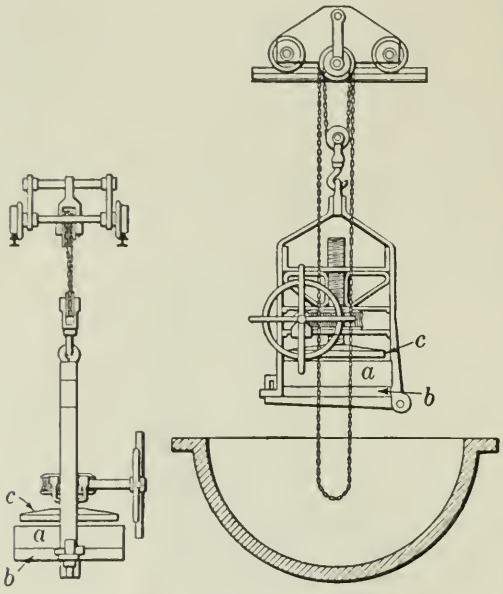


FIG. 102. The Howard press

319. Refining. A vertical centrifugal pump is then lowered into the kettle and the desilverized lead is pumped to the refining furnace. This is a coal-fired reverberatory furnace with a hearth about 13 feet wide, 28 feet long, and $2\frac{1}{2}$ feet deep, holding about 300 tons of lead. Here the lead is held at a temperature of 540° C. for twelve hours. Air or steam is blown through the bath to agitate the metal and oxidize the Zn and other impurities. The Zn, the Pb, and the remainder of the Sb form a layer of mixed oxides, which is skimmed off and returned to the process. The lead, now pure and soft, is cast into pigs for market.

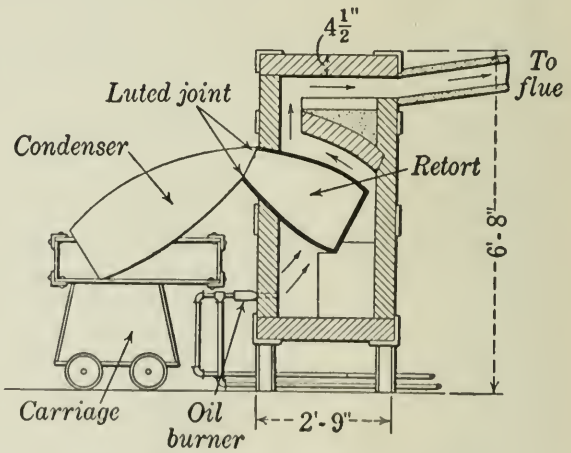


FIG. 103. A distillation furnace

320. Distillation. After the lead is pressed out the zinc skim is charged into a distillation retort, shown in Fig. 103. This consists of a bottle-shaped graphite retort 40 inches high and

19 inches in diameter. The retort is charged with rich zinc crust and a small percentage of charcoal breeze, a graphite condenser is luted over its mouth, and the temperature is raised to about 1100° C. As the zinc distills off and collects in the condenser, it is tapped out through a hole in the bottom and cast into slabs. This zinc is returned to the zincking floor. When all the zinc has been distilled, the condenser is removed, the retort is tilted, and the bullion, containing Ag, Au, and Pb, is cast into bars.

321. Cupeling. The next step is the removal of the lead, which takes place in a cupeling furnace, shown in Fig. 104. It

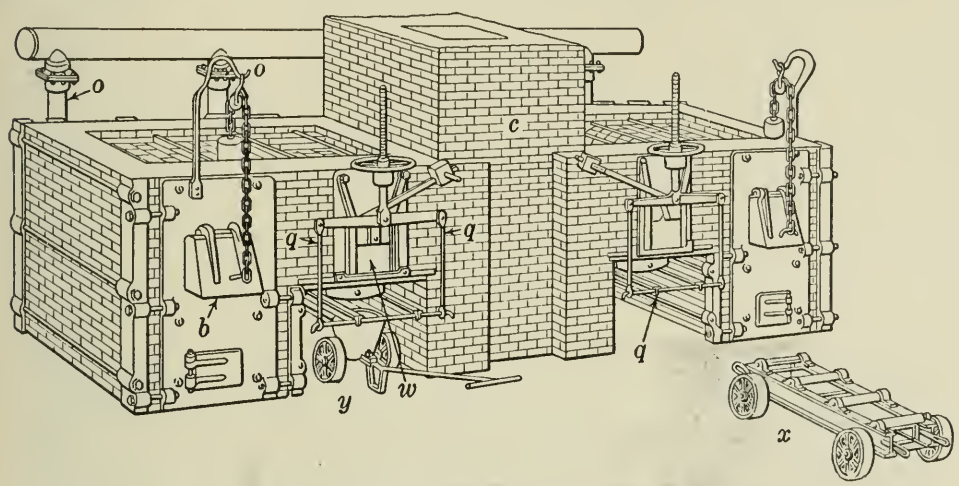


FIG. 104. A cupeling furnace

consists of a hearth, or test, of bone ash or Portland cement mounted upon a truck. This test has a depression holding a bath of molten lead about 3 inches deep. The truck can be run under the furnace and the test raised into position by means of jackscrews. The test is heated by means of fire box *b*. A high-volatile coal is used, so that the long flame may play over the surface of the lead on the hearth. Many modern furnaces are heated by fuel oil, and in that case the burner is inserted in the working door of the furnace. The surface of the molten lead is oxidized to PbO. Impurities such as Cu, Fe, and Zn are also oxidized and enter this litharge slag, which is raked off through the working door *w* into a litharge pot *y*. Air under slight pressure is admitted through tuyère openings in the back of the furnace. Some of the PbO is volatilized and goes up the flue, while a small part is absorbed by the cupel. Lead is fed in as

cupellation goes on, until there is a bath of lead with a high percentage of silver left on the test. The cupellation process is then carried to completion, and a gold-silver alloy is left. This is ladled out and cast into bars each holding 1000 ounces of bullion. Furnaces are often built with twin hearths, as indicated, so that while one is in operation the other can be withdrawn for repairs or renewal. The bullion may be sold to the mint or refined, by acid parting, to pure gold and pure silver.

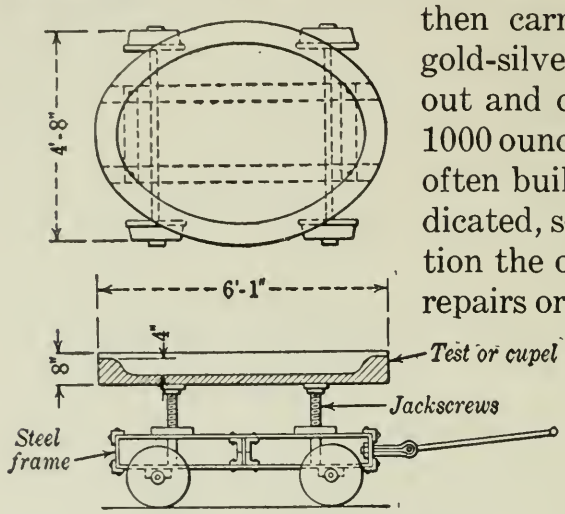


FIG. 105. A cupel, or test

322. Treatment of softener dross. The drosses from the Parkes process may be roughly divided into two classes: those which contain silver and copper and those which do not. The former are smelted in a small coal-fired

FIG. 106. Desilverizing kettles

reverberatory known as a *residue furnace.* The products are residue lead, containing the major part of the lead and nearly all the silver; matte, containing lead, copper, and some silver;

and slag, containing lead, antimony, and arsenic, with almost no silver. Since the dross contains no sulphur, it is necessary to add, besides the suitable fluxes, a little high-grade galena in order to furnish sulphur for the matte.

The residue lead is returned to the head of the process to be treated as new material. The matte may be reduced in a converter but is usually sold to a copper smelter. The slag is added to the dross, which does not contain copper, and is smelted, with the proper fluxes, in a small blast furnace. The products from this furnace are antimonial lead and slag. The former is cast into pigs; the latter goes to waste.

ELECTROLYTIC REFINING OF LEAD

323. Betts process. The Betts process is the only electrolytic process for refining lead that has been successful. It is carried out by the multiple system in much the same way as the electrolytic refining of copper. Cast anodes of lead bullion and cathodes of pure lead are suspended in an electrolyte of lead fluosilicate ($PbSiF_6$) and hydrofluosilicic acid (H_2SiF_6). In the process the $PbSiF_6$, dissolved in water acidulated with H_2SiF_6, is partly dissociated into Pb and SiF_6 ions. Under the action of the electric current the SiF_6 ions travel to the anode, give up their charges, and combine with an equivalent amount of lead. The Pb ions migrate to the cathode, give up their charges, and are deposited as metallic lead. The impurities are left behind on the corroded anode, enter the electrolyte, or drop to the bottom of the tank as a slime or mud. The hydrofluosilicic acid is made from 35 per cent HF and powdered quartz. Lead is dissolved in it to form a solution with from 7 to 10 per cent of Pb and from 8 to 12 per cent of fluosilicic acid. Glue to the amount of 0.1 per cent is added to obtain a firm, coherent deposit on the cathode. In this solution are suspended anodes of base bullion about $1\frac{1}{2}$ inches thick and weighing about 300 pounds. The bath is maintained at a temperature of 35° C. The cathodes are thin sheets of pure lead. They may be cut from sheets of soft lead or they may be electrodeposited on cathodes of steel which have been copper-plated and graphited. The tanks are of wood coated with about $\frac{1}{4}$ inch of petroleum-residue asphalt.

The drop in potential between electrodes is 0.45 volt, and the current density is from 15 to 18 amperes per square foot. The Cu, Bi, As, Au, and Ag remain as a coating on the corroded anode or drop to the bottom of the tank. The Zn, Fe, Co, and Ni enter the electrolyte. This becomes foul after a while, so that a portion must be withdrawn each day for purification, and fresh electrolyte added in its place.

When about 75 per cent of the anode has been corroded it is removed, the coat of impurity scraped off, and the lead recast into new anodes. The cathodes are melted down and cast into bars for market. The anode mud averages 8000 ounces of Ag and Au per ton, chiefly Ag. This is refined by the same processes as described under the refining of copper.

324. Advantages. The advantages of this process are that it furnishes a high yield of refined lead which is free from Bi and that it affords a method of recovering this Bi. Nearly all the lead is recovered in the Betts process, whereas in the Parkes and Pattinson processes there is an unavoidable loss of lead in the slags and flue dust. The disadvantages are that the refined lead contains from 0.20 to 0.30 ounce of Ag per ton as against from 0.11 to 0.12 ounce in the Parkes process, and that the cost of electrolysis is greater than that of zinc desilverization. Its chief use is in preparing very high-grade lead for use in the manufacture of white lead for the paint industry. Lead for other industrial uses, except from high-Bi ores, can be more quickly and cheaply produced by the Parkes process.

325. Casting machine. To meet market requirements lead must be cast in neat, smooth pigs of about 100 pounds weight and stacked neatly in railroad cars. Many smelters or refineries must handle several thousand of these each day, so that casting is quite an item of expense. At the United States Smelting Company Lead Refinery at Graselli, Indiana,* this is carried out on a casting wheel, shown in Fig. 107. This casting wheel, 19 feet in diameter, contains 120 molds about its circumference, divided into 24 groups of 5 molds each. The frame of the wheel rides on rollers supported on a concrete foundation. The pigs are cast from a spout supplied by a centrifugal pump immersed in the drossing kettle. The motion of the wheel is intermittent; there is a pause to permit the pouring of five pigs in one unit

* *Engineering and Mining Journal-Press*, Vol. 124, No. 22.

and the removal of the five pigs from another, which has meanwhile reached the lifting crane. As the wheel moves, the pigs are cooled with water and stamped by a stamping machine, and finally reach the lifting crane. The pigs are then raised in the molds by means of pin ejectors, two for each pig. When the 5-mold unit reaches this crane these pins are engaged by a gently sloping track which raises the pigs in the mold. The crane, on

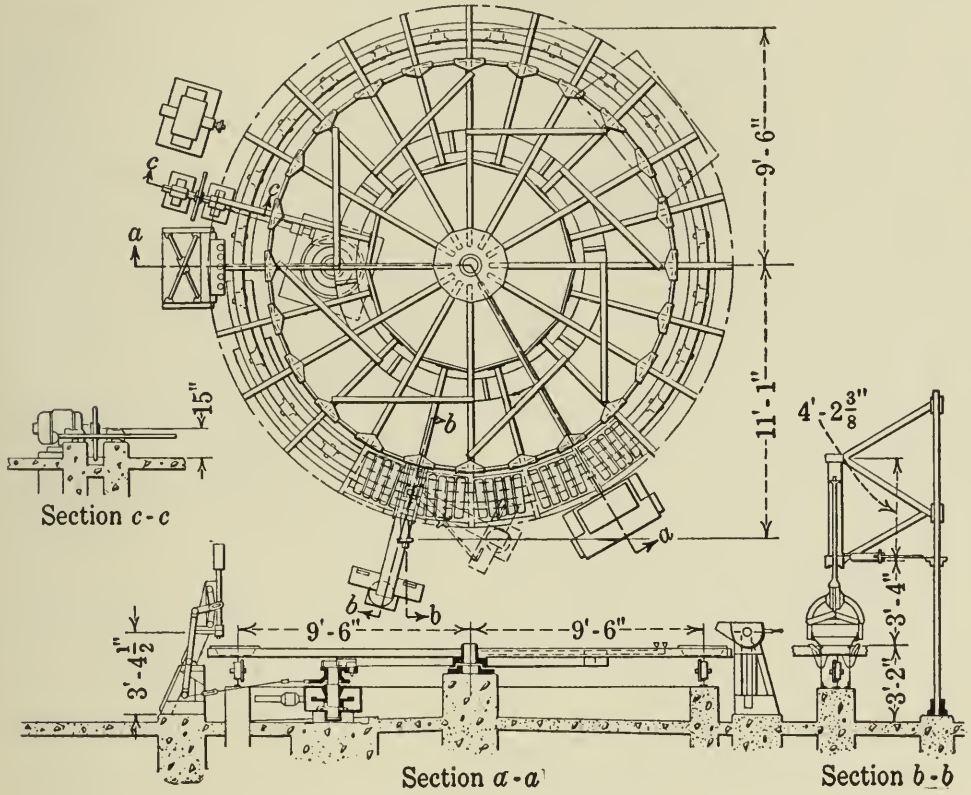


FIG. 107. A casting wheel

the right of the sketch, then takes the pigs in groups of five and piles them on an electric truck, seven deep, for transportation to the railroad cars. The next movement of the wheel disengages the pins from the track, and they drop back flush with the bottom of the mold and are ready for the next pouring.

THE CONCENTRATOR OF THE HECLA MINING COMPANY

326. Crushing. The lead-silver ore from the Hecla mine at Burke, Idaho, is hoisted from the mine and dumped automatically into a tipple bin of 1000 tons capacity. It then undergoes

a preliminary crushing and sorting before the milling grade of ore is sent to the concentrator at Gem, three miles distant. The flow sheet of this crushing and sorting plant is shown in Fig. 108. Briefly, the ore passes over a 5-inch grizzly. The oversize from this is crushed to 5 inches in a Blake crusher. Both products are then sent over 3-inch grizzlies and vibrating screens to the sorting plant. Directly in front of the coarse-rock chute a double line of water sprays washes the oversize on the sorting belts, making the ore more adaptable to hand sorting. The fines washed out in this way are de-slimed by two drag classifiers, the sand going to each shuttle conveyor and the slime overflow to a thickener. The spigot of this thickener is dewatered by an Oliver filter and the cake mixed with the mill feed in the bins. From two 36-inch sorting belts men are able to pick out waste rock low enough in lead and silver to be rejected and rich ore high-grade enough to be sent directly to the smelter. Under ordinary conditions each ore-sorter produces about 12 tons of crude ore, and each waste-sorter about 25 tons of waste per 8-hour shift. The balance of the material is crushed to $1\frac{1}{4}$ inches in a gyratory crusher which feeds a 24-inch shuttle conveyor, in turn discharging into two mill bins having a combined capacity of 3200 tons.

The crushed milling ore has an average composition as follows:

Pb	7.5 per cent
Zn	0.8 per cent
Fe	7.0 per cent
Insoluble	68.0 per cent
Ag	4.0 ounces per ton

It is taken in railroad cars to the mill at Gem, a flow sheet of which is shown in Fig. 109. The mill bin contains 800 tons, and feeds through a scalping trommel into a set of 42 × 16 inch rolls. This crushed material is then trommeled into the following sizes:

Through 35 mm. on 18 mm.
Through 18 mm. on 12 mm.
Through 12 mm. on 7 mm.
Through 7 mm. on 3 mm.
Through 3 mm. on 16 mesh.

327. Gravity concentration. The sized material is then treated on Harz jigs each of which makes its respective concentrate,

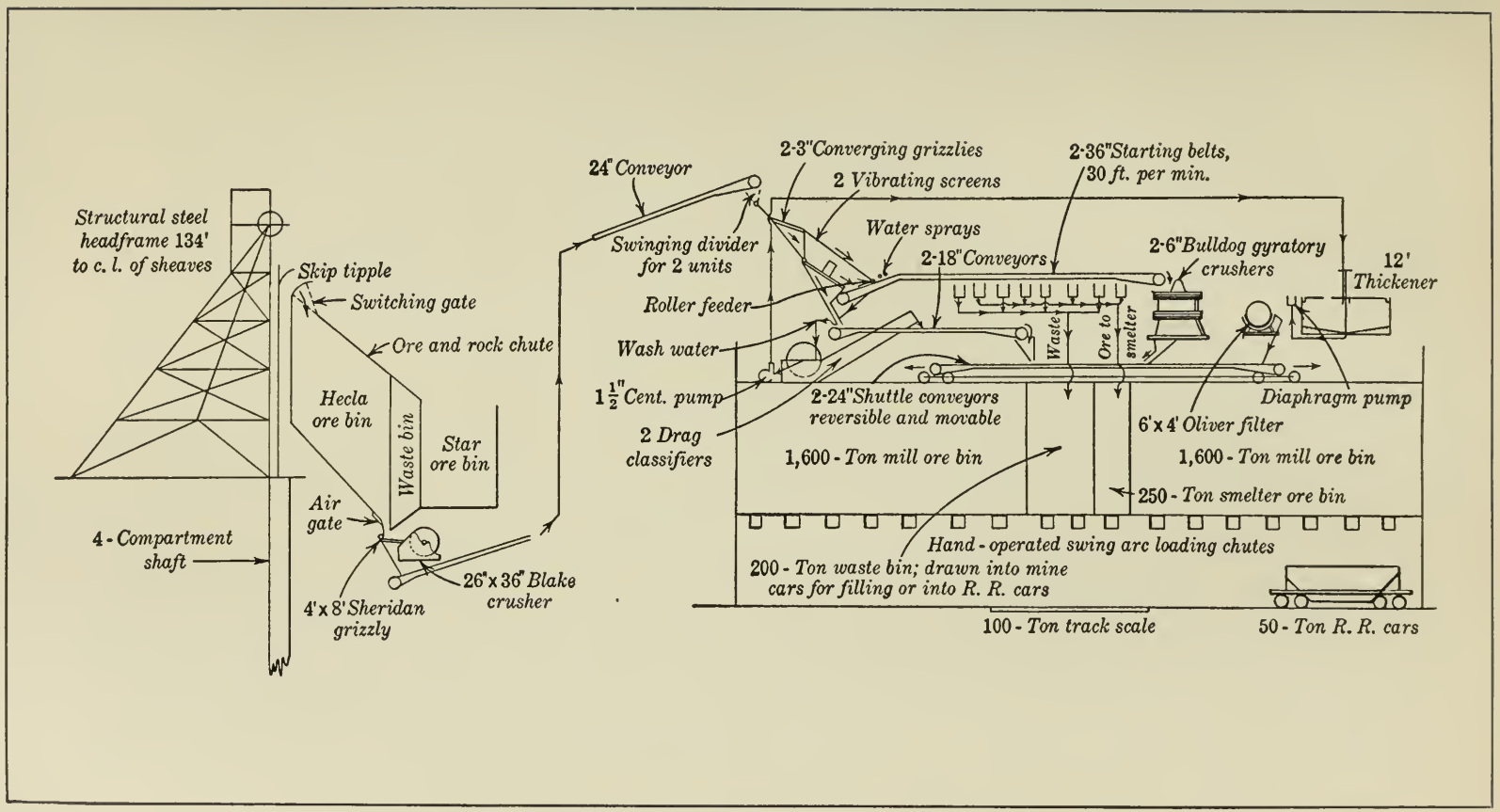

Structural steel headframe 134' to c. l. of sheaves
Skip tipple
Switching gate
Ore and rock chute
Hecla ore bin
Waste bin
Star ore bin
Air gate
4 - Compartment shaft
4'x 8' Sheridan grizzly
26"x 36" Blake crusher
24" Conveyor
Swinging divider for 2 units
2-3" Converging grizzlies
2 Vibrating screens
2-36" Starting belts, 30 ft. per min.
Water sprays
2-18" Conveyors
2-6" Bulldog gyratory crushers
12' Thickener
Roller feeder
Wash water
1½" Cent. pump
2 Drag classifiers
Waste
Ore to smelter
2-24" Shuttle conveyors reversible and movable
Diaphragm pump
6'x 4' Oliver filter
1,600 - Ton mill ore bin
1,600 - Ton mill ore bin
250 - Ton smelter ore bin
Hand - operated swing arc loading chutes
200 - Ton waste bin; drawn into mine cars for filling or into R. R. cars
100 - Ton track scale
50 - Ton R. R. cars

FIG. 108. Hecla crushing and sorting plant

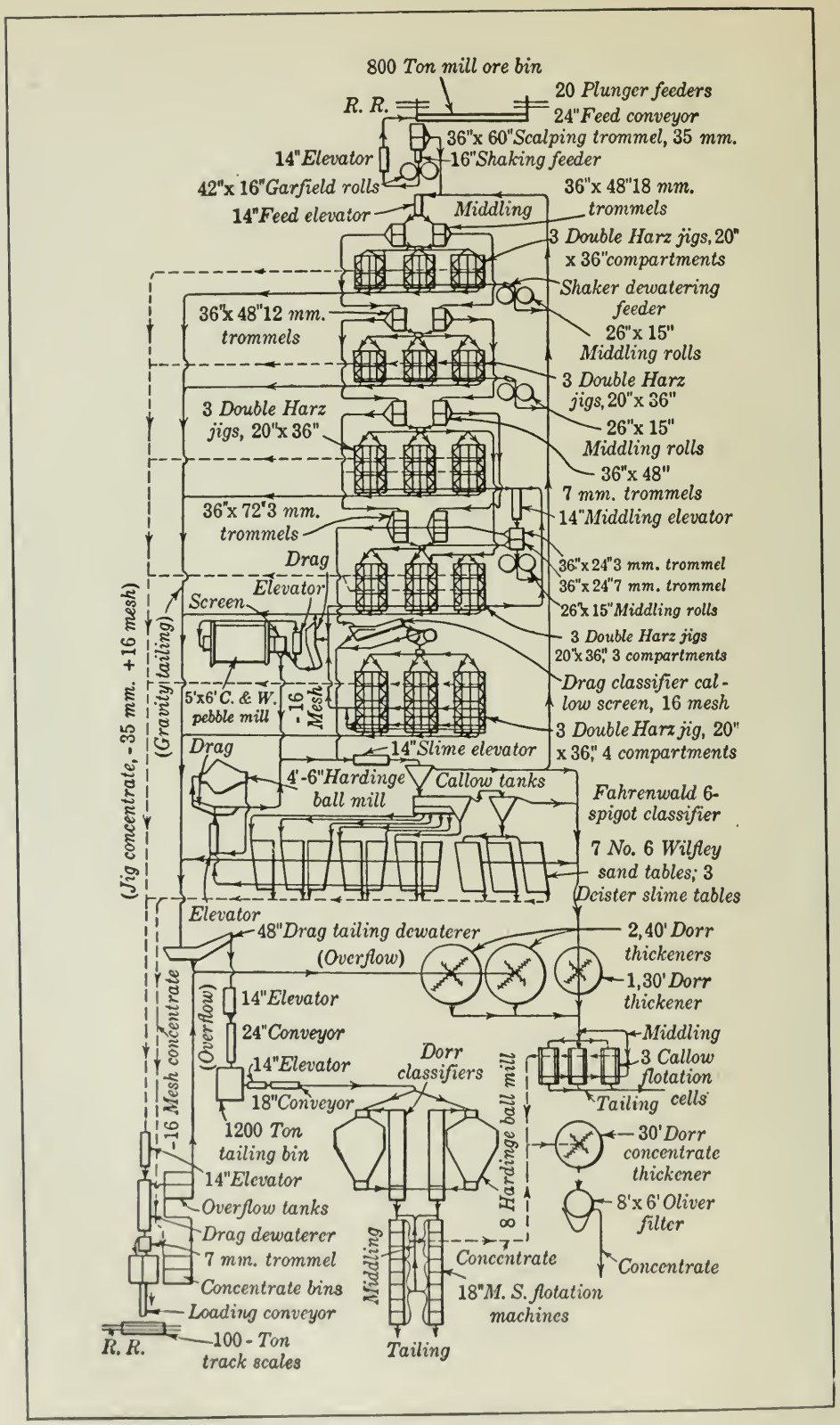


FIG. 109. Flow sheet of Hecla mill

middling, and tailing. The middling is crushed at each stage and returned to the original feed in order to recover the galena in as coarse a condition as possible. All the material passing through 16 mesh is classified in a 6-spigot Fahrenwald constant-density classifier and tabled in the various sizes, making a concentrate, middling, and tailing. Table middlings are ground to pass 150 mesh, and join the original slime, which is tabled on three Deister slime tables, making a clean concentrate. Middlings from the Deister tables are pumped to a 30-foot Dorr thickener. The overflow of the Fahrenwald classifier is thickened in a Callow cone. The spigot of this is treated on Wilfley sand tables; the overflow goes to Dorr thickeners and then to the primary flotation plant, which consists of three Callow cells. The concentrate from these, together with that from the Minerals Separation plant, is thickened and then dewatered in an 8 × 6 foot Oliver filter.

328. Oil flotation. Formerly the tailings were used for road material, track ballast, and concrete work. They are now dewatered in a drag classifier and stored in a 1200-ton tailing bin. These tailings are then ground in two 8-foot Hardinge ball mills, working in closed circuit with Dorr classifiers. This pulp is treated in two 18-inch, 8-cell Minerals Separation flotation machines. Steam-distilled pine oil and cresylic acid in about equal proportions are used, the requirements being about 0.05 pound per ton of feed. The first three cells of each machine produce a lead-silver concentrate which will average about 50 per cent Pb and 34 ounces of Ag per ton. This concentrate is pumped to the thickening and dewatering equipment and treated with the concentrate from the primary flotation plant. All middlings from the last five cells are in closed circuit with the machine. From the overflow weir in the last cell the tailing is discharged to waste. The extent of grinding, as well as the total recovery of lead, is indicated by the following analysis of flotation tailing:

	Per Cent by Weight	Per Cent of Lead
On 28 mesh	Trace	0.10
On 48 mesh	7.5	0.14
On 100 mesh	22.5	
On 200 mesh	16.5	0.13
Through 200 mesh	52.5	
Average		0.13

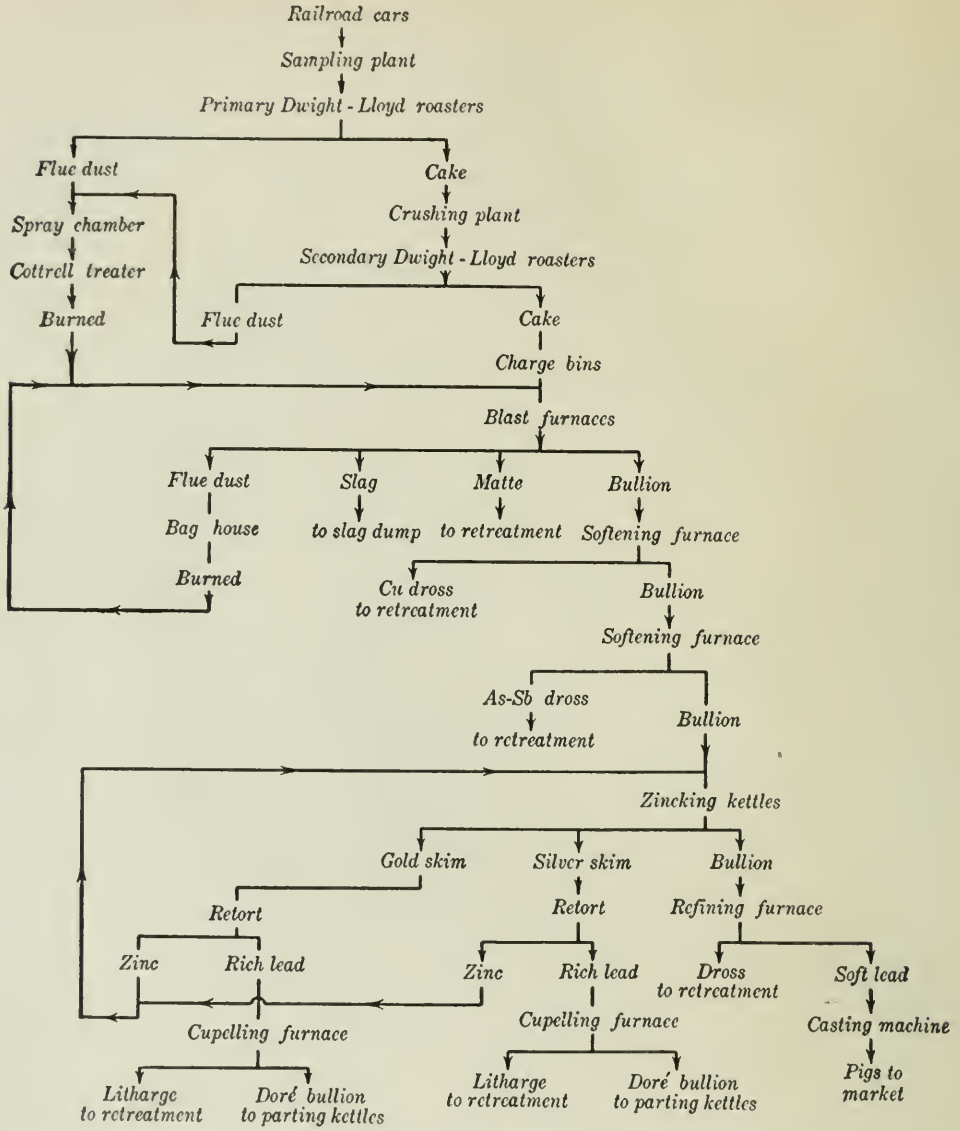


FIG. 110. A flow sheet of the Bunker Hill smelter

At the present time, of the total concentrates produced, 66 per cent is accounted for by the jigs, 14 per cent by the tables, and 20 per cent by flotation. The coarse concentrates are very desirable as blast-furnace feed. The milling cost is slightly under $0.70 per ton.

THE BUNKER HILL AND SULLIVAN SMELTER

329. Ore. The smelter of the Bunker Hill and Sullivan Mining and Concentrating Company, located at Kellogg, Idaho, is a good example of a modern lead smelter. A flow sheet of the

present plant is shown in Fig. 110. While most of the ore is obtained from mines and concentrators operated by the company, a variable and increasing tonnage of custom ore is handled. Under normal conditions the ore receipts consist of approximately 18 per cent of crude ore, 44 per cent of flotation concentrates, and 38 per cent of table and jig concentrates. The feed to the smelter will vary between the following extremes:

	Per Cent		Per Cent
Pb	43 to 47	Fe	10 to 12
S	9	Zn	5
CaO	7	H_2O	3.5 to 5.5

330. Roasting. The roasting plant consists of ten standard Dwight-Lloyd straight-line machines. Five of these are used for primary roasting and five for secondary or final roasting. Roasting must be carefully carried out, for nearly half the charge consists of fine flotation concentrates, which, unless properly sintered, would cause trouble in the blast furnaces. After the primary roast the cake is crushed and re-roasted in the secondary machines. The final product for blast-furnace reduction contains from 1.5 to 2.0 per cent of S. This sinter is then taken in standard-gauge railroad cars to the blast-furnace charge bins.

331. Blast furnaces. The blast-furnace department contains three 48 × 180 inch furnaces similar in design to those already described. Each of these furnaces has a capacity of from 300 to 400 tons of feed per twenty-four hours and produces from 100 to 150 tons of lead bullion per twenty-four hours. From 9 to 12 per cent of coke is used in the charge. The furnace campaign varies from six months to a year, depending upon the character of the ore being treated. The following analyses indicate, by per cent, the average composition of the base bullion and slag:

	Base Bullion	Slag
Pb	97.5	1.0
Cu	1.0	0.12
As	0.15	—
Sb	1.25	—
SiO_2	—	26.0
ZnO	—	10.0
FeO	—	34.0
CaO	—	17.0
Au (ounces per ton)	0.5	Trace
Ag (ounces per ton)	85 to 250	0.10

332. Dust recovery. The flue dust from the blast furnaces is cooled in the connecting flues to about 180° F. and sent to the bag house. The pressure on the system is maintained at about $\frac{1}{2}$ inch of water. The bag house is divided into seven compartments, each of which contains 400 seamless woolen bags 18 inches in diameter and 30 feet long. These bags are automatically shaken every two hours. The dust is caught in hopper-shaped bins and burned, and the sinter is sent back to the blast furnace. The gases from the refinery are also treated in this bag house.

The flue dust from the roasters is first treated in a spray chamber, where it is cooled from a temperature of 150°–250° F. to a temperature of 100°–120° F. It is then sent to the Cottrell-treater plant, which consists of 14 compartments, each of which has 64 pipes 12 inches in diameter and 16 feet long. The pipe forms one electrode and a No. 12 wire the other. The current used is 0.1 ampere at 100,000 volts. Every two hours the current is cut off from a section, and mechanical hammers dislodge the collected dust for two minutes. This is burned in the bins, and the sinter is sent back to the roaster or to the blast furnaces, according to its chemical composition.

333. Refinery. This company treats a tonnage large enough to warrant refining its own gold and silver. Smaller smelting companies frequently find it more economical to sell their product, in the form of doré bullion, to the United States Mint or a large refinery. The furnace bullion is first softened, two drosses being removed — one of copper and one of arsenic and antimony. The softened bullion is then zincked in 5 × 10 foot kettles. The gold dross, taken off first, contains all the gold and from 10 to 20 per cent of the silver. More zinc is added, and the silver dross, which contains the remainder of the silver and only a trace of gold, is removed. These two drosses are sent on to be retorted and cupeled separately. The zinc-bearing bullion is then refined in an 11 × 22 foot reverberatory furnace, the dross is returned to the process, and the soft lead is cast into pigs for market. This plant produces each month about 6000 tons of desilverized lead, 125 tons of antimonial lead, 500,000 ounces of silver, and 2000 ounces of gold.

TOOELE PLANT OF THE INTERNATIONAL SMELTING COMPANY

334. Location. The Tooele plant of the International Smelting Company is situated about five miles east of Tooele City, Utah. The plant consists of a lead-zinc flotation concentrator, a copper smelter, and a lead smelter. The plant treats lead, lead-zinc, copper, and dry silver ores and produces blister copper, lead bullion, and zinc concentrates. Lead-zinc ores are received mainly from Park City and Bingham, Utah, and from Colorado, Nevada, and Idaho; lead ores are received mainly from Tintic, Park City, Idaho, and Nevada; and copper concentrates are received mainly from California, Idaho, and Utah. For the purposes of this chapter only the lead section of the smelter will be discussed.

335. Sampling. As indicated in Fig. 111, all ores are weighed on track scales and dumped into the receiving bins at the sampling mill. A grab sample is taken in order to determine the character of the ore for fluxing requirements, all settlements being made on the basis of the mill sample. From the sampling mill the ore is delivered by belt conveyor to the bin designated by the department head concerned. These bins have a capacity of 13,000 tons. The sampling mill is so arranged that screening may be carried out in order to separate the lead ores into a coarse product for blast-furnace treatment and a fine product for the sintering plant.

336. Sintering plant. The sintering plant consists of ten standard Dwight-Lloyd sintering machines (42 × 264 inches), each capable of producing about 125 tons of sinter per twenty-four hours at a pallet speed of 20 inches per minute. The depth of charge on the pallets is approximately 6 inches. The proportions of silica and iron in the charges are controlled by the lead-plant metallurgist according to the available ore supply and the required slag at the blast furnaces. In case it is necessary to eliminate more sulphur than is possible in a single treatment at the Dwight-Lloyd plant, the charge is crushed and treated again over the machines. For example, a mixture of concentrates, flue dust, and ore containing approximately 15 per cent of sulphur is fed to certain machines termed pre-sinter machines. On these machines a high sulphur elimination is made,

but the product is not low enough in sulphur nor of the right physical structure to go to the blast furnaces. This material is ground and mixed with other charge products and re-treated on "finish-sinter" machines. In 1927 these finish-sinter machines were treating a charge containing approximately 11 per cent of sulphur and producing a sinter of the following composition:

	Per Cent
Insoluble	25.0
Fe	18.0
CaO	3.0
Zn	3.5
S	2.7
Pb	26.0
Cu	1.5

The sinter from the Dwight-Lloyd machines is delivered to railroad cars and dumped to blast-furnace charge bins, as shown on the flow sheet. The air and gas drawn through the charge bed contains flue dust and fume of value and is treated in a Cottrell installation for removing these values. The fume and dust from this Cottrell are returned to the Dwight-Lloyd charge.

337. Blast-furnace plant. The Tooele furnace installation consists of five furnaces 54 inches wide at the tuyères and 180 inches long, each capable of treating 265 tons of charge per twenty-four hours. The distance from the charge floor to the tuyère line is 24 feet 8 inches. Air at approximately 40 ounces per square inch of pressure, 6000 cubic feet per minute, is delivered through twenty-five tuyères to the furnace.

The various materials making up the blast-furnace charge are delivered by cars or belt conveyors to the blast-furnace scale or weighing bin, as shown on the flow sheet. The coke for fuel is contained in a steel tank equipped with scale or weighing hoppers. A 4-ton charge is made up from the various bins. This charge usually consists of about 70 per cent of sinter and the remainder of limestone, siliceous ores, and plant by-products, no barren iron-ore flux being used. Scrap iron in varying amounts is added to this charge before it is dumped into the furnace. Approximately 14 per cent of coke is used.

There are four products made in the blast furnace: lead, lead-copper matte, slag, and fume and flue dust. The fume and flue dust are filtered from the gas passing from the furnace in a

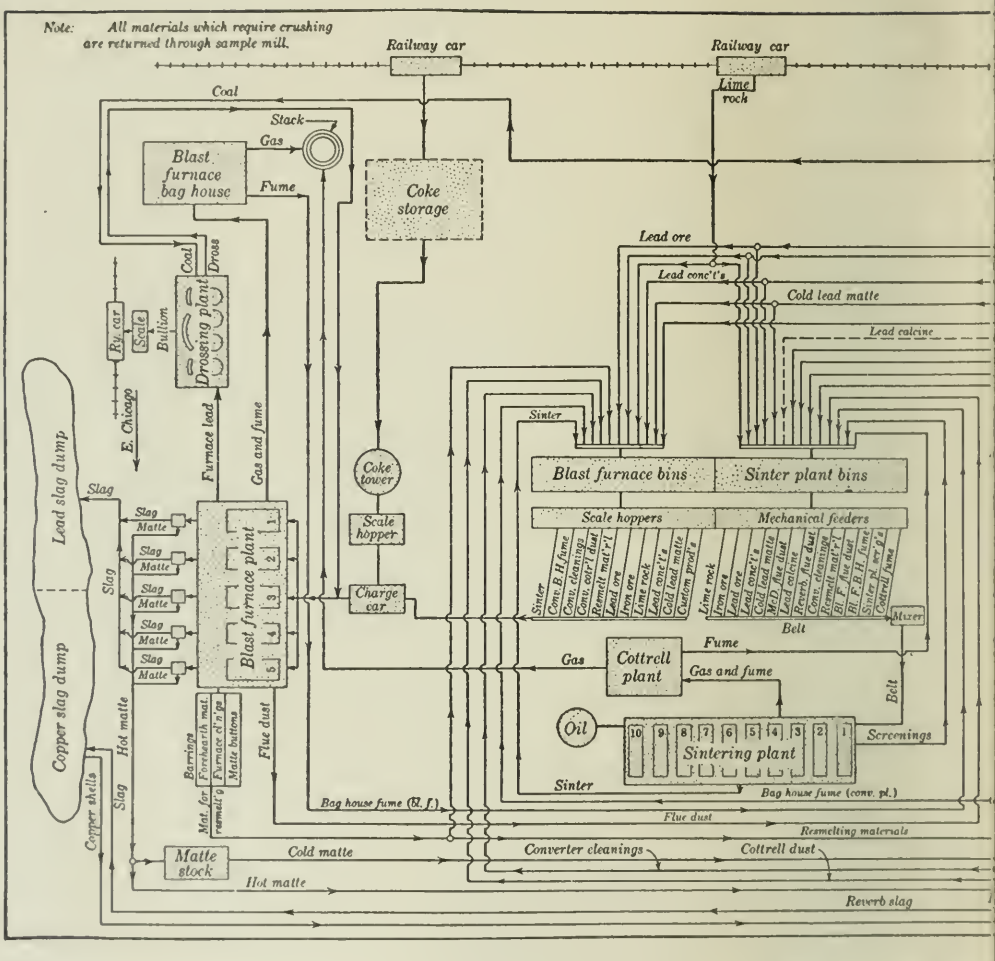
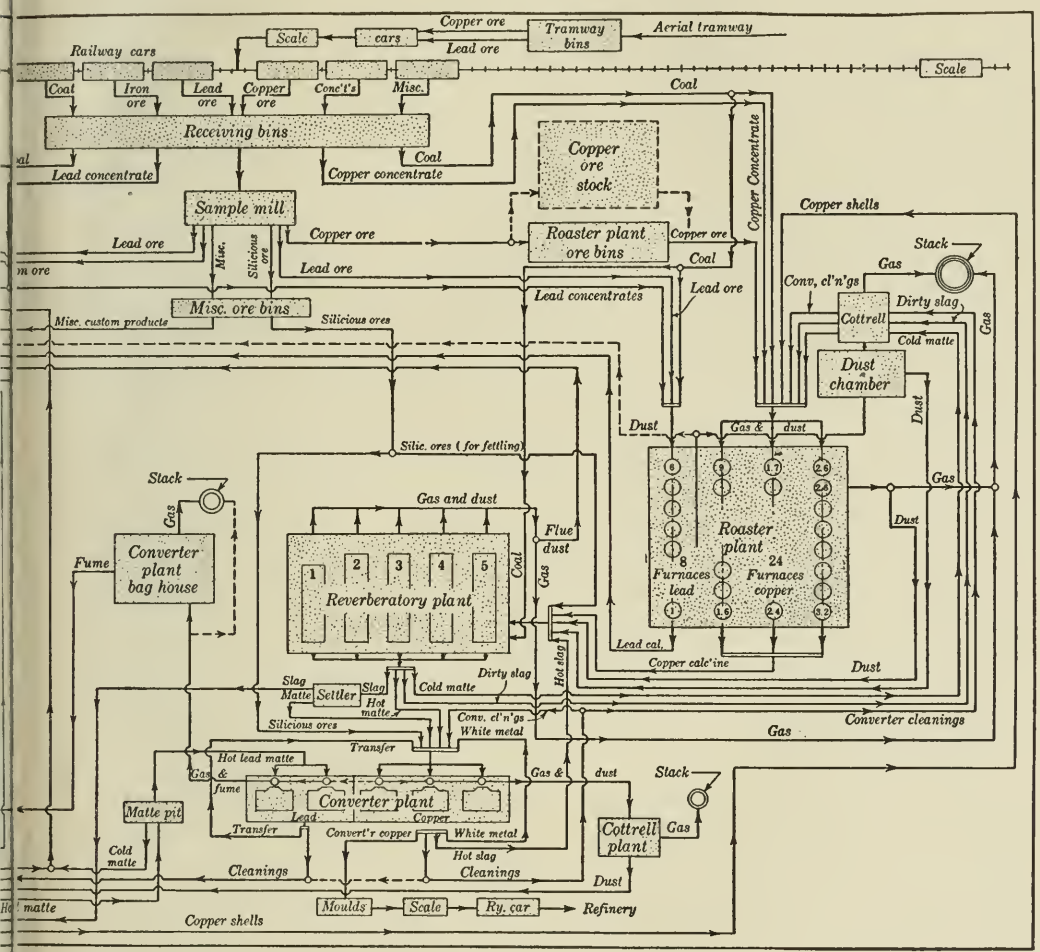


FIG. 111. Flow sh



t of Tooele smelter

bag house. The recovered fume is returned to the sintering plant or to the blast-furnace charge, according to plant conditions. The furnace lead is delivered to drossing kettles, where the copper and arsenic content is greatly reduced. The lead is cast into 90-pound pigs for shipment to the refinery at East Chicago. The cast lead contains the major part of the recovered silver and gold contained in the ores. The lead-copper matte, ordinarily containing 20 per cent of copper, 10 per cent of lead, and the remainder of the gold and silver, is delivered hot to the converter plant, where it is treated exactly like a copper matte except that the gas from the converter is filtered in a bag house in order to recover the lead. The copper is blown into blister copper and shipped to an electrolytic refinery in New York. The lead recovered in the converter bag house is returned either to the blast furnace or to the sinter plant, according to plant conditions. The converter slag is returned to the sintering plant. The blast-furnace slag is taken to the dump in slag pots. It is approximately of the following composition:

SiO_2	36.0 per cent
Fe	32.0 per cent
CaO	20.0 per cent
ZnO	5.0 per cent
Pb	0.8 per cent
Cu	0.15 per cent
Ag	0.25 ounce per ton

HYDROMETALLURGY OF LEAD

338. General. It has been pointed out that the successful reduction of lead in either the ore hearth or the blast furnace requires an ore or concentrate containing from 30 to 60 per cent of lead. Most of the lead ore now being mined is of low grade, of the order of from 6 to 10 per cent Pb. It follows, then, that some hydrometallurgical method would dispense with the inefficient concentration process and the costly smelting process and produce lead cheaply and quickly. Unfortunately research has so far failed to give us any such process that can compare with the leaching methods for zinc, gold, and silver. Many are in the experimental stage, but few have passed beyond the small plant of 50 tons daily capacity.

339. Raw materials. Electrolytic-zinc-plant tailings often contain lead and small amounts of Au and Ag. It is too low-grade for treatment in a lead blast furnace, nor can it be successfully cyanided for the precious metals. There are large tonnages of this material available for treatment.

Flue dust from lead smelters and zinc smelters is not well adapted to smelting, owing to its chemical composition and its physical condition.

Ores of lead containing the sulphate and carbonate are difficult to concentrate, owing to the brittleness of the minerals and to the fact that they are not amenable to the oil-flotation process.

Tailings from lead-concentrating plants are too low-grade for further concentration, but being in a fine state of division they offer an admirable product for leaching.

Many complex lead-zinc-silver ores are not amenable to flotation, and although we have large deposits of such ores, they cannot now be treated.

340. Conversion to soluble form. Most of our lead is derived from sulphide ores. So far no suitable reagent has been found for dissolving this lead sulphide directly, — at least none cheap enough for commercial use. It is necessary to change this lead into a more soluble form — the sulphate, carbonate, or chloride — before leaching. The sulphate and chloride are soluble in brine; the carbonate in acidified brine.

Sulphide ores can be easily and completely converted into the sulphate by a low-temperature roast (from 400° to 550° C.). Sulphuric acid treatment has been suggested. It has possibilities, for some of the other sulphides, notably zinc, are not easily sulphatized.

Chloridizing may be carried out by roasting in the presence of salt and by treatment with HCl or ferric chloride.

341. Leaching. Lead chloride, lead sulphate, and silver chloride are dissolved by a neutral saturated solution of NaCl or a strong solution of $CaCl_2$ or $MgCl_2$. Some processes use a little excess chlorine, and where silver chloride is being leached it is necessary to add ferric chloride or acid to dissolve any metallic silver or sulphide which may be precipitated by other sulphide minerals. Ferrous chloride at a temperature of 90° C. will dissolve small amounts of lead chloride.

342. Precipitation. Sponge iron will precipitate lead from brine solutions at ordinary temperatures. Electrolysis with both soluble and insoluble anodes is possible. Chemical precipitation with zinc hydroxide, sodium carbonate, or sodium sulphide has been patented. At the present time the commercial plants are using either electrolysis or sponge iron.

343. Consolidated Mining and Smelting Company. This company operates a large electrolytic zinc plant. The residues from this plant contain up to 24 per cent of Pb and several ounces of Ag per ton. It is not a desirable product for blast-furnace smelting, but does lend itself admirably to leaching.

In an experimental plant the residue was mechanically agitated in a warm, slightly acid brine solution (from 1 to 2 grams of H_2SO_4 per liter). After forty-five minutes of agitation nearly all the lead and about 78 per cent of the silver were dissolved. The pulp was then thickened in a Dorr thickener and filter-pressed in an American filter to yield a solution containing from 9 to 10 grams of Pb and from 1 to 2 grams of H_2SO_4 per liter. The cake was not washed to any great extent, since it would unduly dilute the rich solution. The silver was precipitated with scrap iron. The resulting solution was then electrolyzed with iron anodes and cathodes 1.5 inches apart. The bottoms of the electrolytic tanks were porous in order that air might be bubbled through the solution to dislodge the sponge lead from the cathodes. The drop in potential between electrodes was from 1.0 to 1.5 volts, and the current density was 15 amperes per square foot. From 12 to 15 pounds of lead was precipitated per kilowatt hour at an electrode consumption of 0.3 pound per pound of lead. The sponge lead was briquetted and melted. While the process was technically successful, with a recovery of about 93 per cent of the lead and 75 per cent of the silver, it was found more economical to treat the zinc-plant residues in the blast furnaces so long as the Pb content of these was above 18 per cent.

344. Tainton lead leach and electrolytic precipitation. The Bunker Hill and Sullivan Mining and Concentrating Company, at its property at Kellogg, Idaho, now has in operation a small plant using the Tainton lead-leach and electrolytic process, which according to last accounts is making an excellent recovery of the lead and silver. The material now being treated

is a tailings dump from previous water-gravity concentration. The tailings average 1.2 per cent of Pb, 1.0 per cent of Zn, and 0.5 ounce of Ag per ton. These are treated by bulk flotation and yield a product averaging 13.5 per cent of Pb, 9.0 per cent of Zn, and 6 ounces of Ag per ton. Owing to the fact that they have been exposed to the weather for a number of years the lead minerals are partly sulphidized and partly oxidized. The

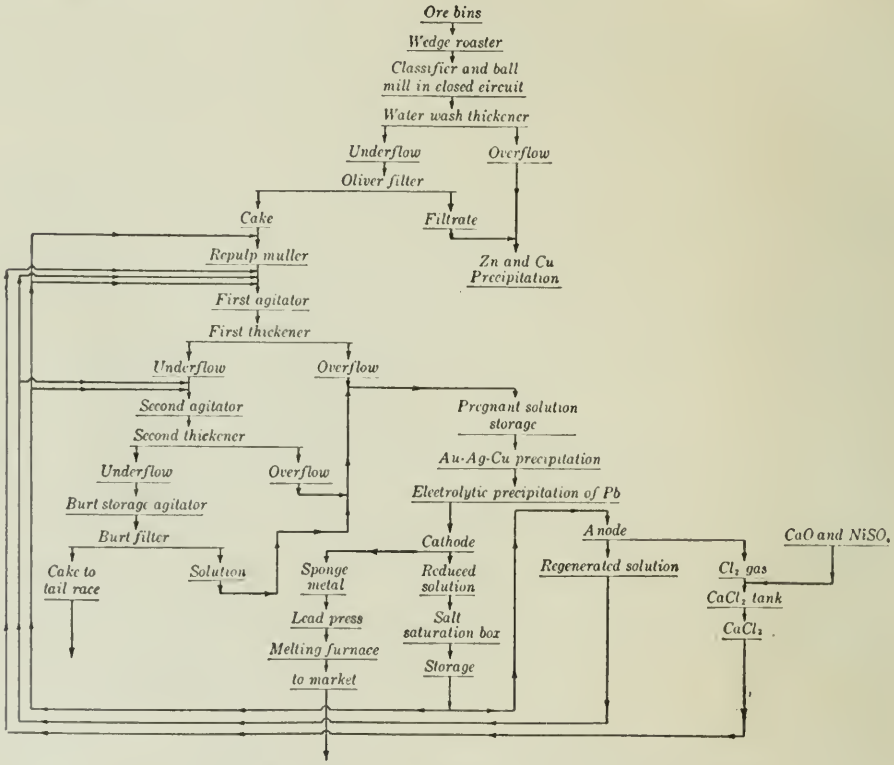


FIG. 112. A flow sheet of the Tainton lead plant

flow sheet of the process is shown in Fig. 112. The concentrates from bulk flotation are first roasted in Wedge roasters. Investigations have shown that at a certain critical temperature (from 450° to 500° C.) the lead is almost completely sulphatized. About 2 per cent of NaCl is added to the roasted ore. If the temperature of the furnace rises too high, the lead and silver are rendered insoluble, probably through the formation of lead silicates. This calls for rather close pyrometric control.

When roasting is complete, the calcines are sluiced with water into a thickener, where the various sulphates, principally those of Mn, Cu, and Zn, are dissolved. After thickening, the

pulp is further dewatered by means of an Oliver filter, a water wash displacing all but a little of the solution. The cake from the Oliver filter is agitated with return electrolyte in a mechanical device, since air agitation would be undesirable owing to the presence of chlorine. The solution contains a mixture of the chlorides of Na, Ca, and Fe, together with a little free chlorine and hypochlorous acid. The sodium chloride converts the lead and silver sulphates to chlorides, thus:

$$PbSO_4 + 2\,NaCl = PbCl_2 + Na_2SO_4,$$
$$Na_2SO_4 + CaCl_2 = 2\,NaCl + CaSO_4.$$

A good deal of trouble was at first encountered, since the oxides of Cu and Zn were also converted. The $CaSO_4$ precipitates in the pulp. A series treatment in a second agitator with the intermediate continuous thickening is indicated in the flow sheet. After filtration the residue is sluiced to the tailrace, while the filtrate goes to the storage for pregnant solution.

The precipitating apparatus is one of the ingenious features of the process. The cell is so constructed that the anode and cathode compartments are separated by diaphragms. The solution passes, first, through the cathode compartment, where lead, carrying silver and gold, is precipitated, and then through the anode compartment, where it picks up free chlorine formed by the decomposition of lead chloride. The anodes are graphite; the cathodes steel disks 22 inches in diameter, revolving at a speed of 125 revolutions per minute in the electrolyte. The lead comes down in the metallic, crystalline form instead of as the soft, black sponge which is obtained on stationary cathodes. Every fifteen minutes, by means of an automatic switch, the rotation of the cathodes is stopped for a few seconds, so that a thin layer of spongy lead is formed. This interrupts the growth of the crystalline lead and causes it to be continually detached by the friction of the solution and carried out of the cell in the form of little granules. The effluent solution, carrying with it this precipitated lead, flows to a drag classifier, where the granules are removed. After washing, these are briquetted and melted to form bullion.

Part of the chlorine liberated from the anode compartments is not used in the solution. This is conducted to scrubbing towers, where it is absorbed by milk of lime. The recovery of

the process ranges from 90 to 95 per cent of the silver and from 95 to 98 per cent of the lead.

The brine leach described above worked very well so long as the lead content of the solution was high. The accumulation of zinc chloride caused the zinc to precipitate with the lead. The solution has since been changed to sodium hydroxide with a little sodium cyanide. Very little zinc is dissolved, but the lead goes into solution as the plumbite. The cyanide serves to dissolve silver precipitated in the brine cells. With this solution the character of the lead deposit changed so that a good deal of difficulty was experienced, because large balls built up in the cell and because both the oxide and the peroxide of lead precipitated out on the anode. At the present time an open-tank cell similar to that used in the deposition of zinc and copper is being employed. Wooden frames hold the diaphragms, steel cathodes, and lead anodes. There are two separate discharge ports for the anode and cathode product. Each anode and cathode has a separate feed. The anodes are stationary, but the cathodes have an up-and-down movement of about $2\frac{1}{2}$ inches. These strokes are at the rate of 50 per minute for about fifteen minutes; then at the rate of 150 per minute for a few seconds. Between these changes the movement is stopped for a few seconds, for the same reason as in the case of the brine-solution precipitation.

345. Tintic Standard process. The Tintic Standard Mining Company employs a modification of the Augustin process (chloridizing roast and brine leach). This is described in Chapter XI.

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CHAPTER IX

ZINC

346. History. Prehistoric races were certainly unacquainted with zinc, owing probably to their inability to maintain the high temperatures and reducing atmosphere necessary for its reduction from common ores. The Romans used this metal as early as 200 B.C., and an idol of zinc found in a Dacian settlement must belong to an even earlier period. It is held that the Chinese were the first to reduce the metal from its ores, for it was from China that the art of smelting zinc ore was brought to England in 1743. Since 1820 the zinc industry has been well established in Europe, with metallurgical centers in Germany and Belgium. In the United States the first zinc was produced in 1835, at the Navy Yard in Washington, D.C., and in 1850 the present New Jersey Zinc Company started operations. Today the United States is the leading producer of this metal.

347. Physical properties. The metal has a bluish-white color and a specific gravity of from 7.04 to 7.14. It is harder than tin and softer than annealed copper, having a scratch hardness of 2.5. At ordinary temperatures it is brittle, being easily broken by striking with a hammer. At 100°–150° C. it becomes so malleable that it can be rolled into sheets or drawn into wire. At 200° C. it again becomes so brittle that it can be pulverized. The tensile strength of zinc varies from 8000 pounds per square inch for the coarse cast metal to 30,000 pounds per square inch for the drawn or rolled product. The melting point is 419.4° C. and the boiling point 907° C.

348. Chemical properties. The atomic weight of zinc is 65.38. Dry or pure air does not affect the metal, but moist air, or that containing considerable CO_2, forms a coating of the basic carbonate. This film protects the metal from further corrosion. At 500° C., in the presence of air, zinc burns to ZnO with a characteristic bluish-white flame. The best solvents of zinc are dilute H_2SO_4 and HCl. It is electropositive to all heavy metals and precipitates these from their solutions.

349. Economic situation. The United States is now the largest single producer of zinc or spelter and the largest consumer of the metal in the world. The production of other countries is shown in Table XXXV. Economic factors, rather than metallurgical developments, have determined the location of the zinc smelters adjacent to supplies of cheap fuel, for the distillation process requires very large quantities of fuel. The largest zinc-producing centers of the world are (1) Upper Silesia, (2) Rhineland and Westphalia, (3) Belgium, and (4) Kansas, Oklahoma, and Illinois. Most of our smelters are situated near the center of a large natural-gas field. The American industry is a highly competitive one and not dominated by any single producer.

350. Marketing and prices. Zinc is marketed in the form of slabs weighing from 40 to 50 pounds. These are generally grooved so that they may be more easily broken into smaller pieces for convenience in making up alloys. The United States produces about 45 per cent of the world's supply of this metal — not quite enough to care for our own needs. As a matter of fact, until the outbreak of the World War this country exported but little zinc. This was due to the fact that our smelters are not favorably situated for assembling foreign ores and conducting a bonded smelting business. Our ores, too, are no more than sufficient to supply our normal needs. The European smelters, on the other hand, are located at or near the seaboard and bring their ores from points as far distant as British Columbia and Australia.

The marketing of zinc ores is largely a matter of arrangement between the miner and the smelter. Schedules vary between wide limits. Ordinarily the base is 60 per cent Zn for sulphide ores and 40 per cent Zn for oxide ores. Bonuses are paid for purer ores, while penalties are inflicted for lower-grade ones or those containing more than stipulated percentages of Cd, Fe, or Pb. Quotations of ore are usually made on Joplin, Missouri, or Platteville, Wisconsin.

The various grades of commercial zinc are described on page 260. Prices are usually given in cents per pound or dollars per hundred pounds, and the principal basing point is East St. Louis, Illinois.

The price range of slab zinc and zinc ore over a period of years is given in Table XXXVI.

Table XXXV. World's Production of Zinc (in Metric Tons)

	1910	1915	1919	1920	1921	1922	1923	1924	1925	1926
Belgium	190,233	51,660	19,860	84,260	66,150	112,290	147,040	162,990	171,890	190,216
Canada	—	—	11,182	16,798	24,035	25,204	27,238	24,896	34,910	55,999
Germany	251,046	186,851	148,000	95,758	27,070	34,800	32,175	41,400	58,623	68,292
Spain	—	8,117	16,310	9,647	6,738	6,269	10,922	12,300	14,500	16,061
Tasmania	560 *	5,393 *	3,727	5,911	1,708	23,896	40,895	47,360	46,521	48,029
United States	269,184	444,082	422,520	420,365	181,894	320,047	463,066	468,262	536,090	555,186
France	65,191 †	19,180	10,800	19,655	30,000	39,716	49,334	55,599	70,000	72,455
Poland	9,514 ‡	2,000 ‡	4,416	5,361	69,956	84,700	96,136	92,176	114,324	124,094
All others	107,318	120,717	69,551	56,741	35,654	59,286	80,366	92,762	100,603	89,080
Total	893,046	838,000	706,366	714,496	443,205	706,208	947,172	997,745	1,147,461	1,219,412

* Australia alone. † France and Spain. ‡ Russia.

Table XXXVI. Prices of Zinc Ore and Metal

Year	Blende Ore per Short Ton	Prime Western Metal per Pound
1910	$40.42	5.370 cents
1916	84.72	12.634 cents
1919	43.40	6.988 cents
1920	47.01	7.671 cents
1921	24.49	4.655 cents
1922	36.54	5.716 cents
1923	41.37	6.607 cents
1924	42.00	6.344 cents
1925	52.76	7.622 cents
1926	50.50	7.337 cents
1927	40.73	6.242 cents

COMMERCIAL ZINC

351. Grades. *Spelter* is the term commonly applied to commercial zinc. In the United States four grades of primary metal are distinguished according to the amounts of Cd, Fe, and Pb which they contain.

High-grade spelter is used for brass that is to be spun or drawn. It should contain not more than 0.07 per cent of Cd, 0.03 per cent of Fe, and 0.07 per cent of Pb.

Intermediate spelter is used for brass that does not need to be of high ductility. It should contain not more than 0.50 per cent of Cd, 0.03 per cent of Fe, and 0.20 per cent of Pb.

Brass Special spelter is used for the better grades of brass that does not need to have much ductility. It should contain not more than 0.75 per cent of Cd, 0.08 per cent of Fe, and 1.00 per cent of Pb.

Prime Western spelter is used for the lower grades of brass and for certain galvanizing operations. It should contain not more than 0.75 per cent of Cd, 0.75 per cent of Fe, and 2.00 per cent of Pb.

Besides primary spelter there is sold in this country a great deal of secondary metal derived from the treatment of scrap, drosses, etc. This metal is usually very impure and may contain as high as 5 per cent of Fe and 3 per cent of Pb. In recent years the amount of secondary spelter has amounted to as much as 23 per cent of the total production.

352. Uses. The principal uses of metallic zinc are in the manufacture of brass and in the galvanizing industry. Table XXXVII indicates some of the other uses and the tonnages involved.

TABLE XXXVII. CONSUMPTION OF SPELTER IN THE UNITED STATES (1924)

	SHORT TONS
Galvanizing	
Sheets	122,900
Tubes	50,300
Wire	29,000
Wire cloth	7,100
Shapes	30,700
Brass-making	178,000
Sheet zinc	61,000
Other purposes	56,000
Total	535,000

Blue powder and zinc oxide are used as precipitating and reducing agents, in the manufacture of rubber tires, as paints, and as raw material for the manufacture of chemicals.

Aside from the brasses the zinc alloys are not of much importance. In small quantities zinc is present in German, or nickel, silver and zinc duralumin.

353. Effects of impurities. In practice Cd, Fe, and Pb are the only foreign metals considered in classifying commercial zinc, since the other metals are present in such small amounts that they do not have any serious effect on the physical or chemical properties of the metal.

The effect of Cd is to harden the zinc and make it more brittle. This effect is more marked at high temperatures (hot-shortness). In galvanizing, zinc practically free from Cd is demanded, as relatively small percentages of this element cause the coatings to crack or peel off when the sheet or wire is bent. For rolling purposes 0.25 per cent of Cd is permissible; as much as 0.5 per cent makes rolling impossible. Cd in brass weakens the alloy and causes it to crack.

In general the effect of Pb on zinc castings is to make them brittle. This becomes noticeable at about 0.7 per cent. In galvanizing, it weakens the coat and causes it to peel or crack. For ordinary brass as high as 0.9 per cent of Pb is permissible, but for brass that is to be drawn or worked, such as that for cartridge cases, even 0.1 per cent is undesirable.

The effect of Fe is to increase the hardness and brittleness of the metal and thus reduce its malleability. In rolling, as little as 0.12 per cent interferes with the work. The presence of Fe indicates careless work in the reduction of the metal, for it is relatively easy to make zinc free from Fe, using ores containing as high as 8 per cent of Fe.

The effect of As and Sb is to make the zinc harder, that of the former being more marked than that of the latter. As little as 0.02 per cent As is noticeable if the metal is to be rolled.

ORES OF ZINC

354. Minerals. The minerals which make up the ores of zinc are few in number. Most of the spelter of the United States is derived from sphalerite (ZnS), although locally deposits of

franklinite, calamine, and smithsonite may be of importance. The present process of reduction of zinc ores requires a very high-grade material; hence most of the domestic ores must be concentrated before they can be smelted. Lead and iron cause difficulties in both the electrolytic and the distillation process, so that many of our ores must be purified before they can be so treated.

Sphalerite (ZnS) when pure contains 67 per cent Zn. The ordinary (resin-colored) blende contains little Fe, but some of the darker varieties contain as high as 10 per cent. Sulphides of Fe, Cu, Cd, As, and Sb are associated with the blende. Fe and Cd are especially injurious, since the former tends to slag the retorts and the latter cannot be separated from the zinc by distillation and detracts from the physical properties of the metal. Blende ores are, as a rule, low-grade. The average ore mined in the United States contains about 5 per cent Zn. Such ores must be concentrated until they contain from 33 to 58 per cent of Zn. Table XXXVIII gives analyses of both pure and complex blende concentrates:

TABLE XXXVIII. ANALYSES OF ZINC CONCENTRATES (IN PER CENTS)

	JOPLIN, MISSOURI	UTAH	IDAHO	MONTANA
Zn	58.260	46.00	38.80	53.90
Cd	0.304	—	—	—
Pb	0.700	1.86	10.00	1.53
Cu	0.049	1.54	—	2.82
Fe	2.230	7.40	13.50	4.40
SiO_2	3.950	4.10	8.50	3.60
S	30.420	30.40	19.30	—
As	—	0.52	—	0.55
Ag (ounces per ton)	—	—	—	16.04
Au (ounces per ton)	—	—	—	0.04

Calamine ($Zn_2(OH)_2SiO_3$) is a white mineral containing 57.1 per cent of Zn. It is characteristic of superficial deposits and is an alteration product of the sulphide. Deposits of it are not important. Most of these are used for the manufacture of ZnO rather than the metal.

Smithsonite ($ZnCO_3$) is another alteration product of the sulphide. It is a white mineral and contains 52.14 per cent of Zn. It is especially desirable as an ore, since it requires no roasting

but can be retorted directly. The large deposits of this mineral have long since been exhausted. It is rare in this country but common in Europe.

Zincite (ZnO) and *franklinite* ($ZnO \cdot MnO \cdot Fe_2O_3$) are relatively unimportant, since they are found in only one locality in the United States, — at Franklin Furnace, New Jersey. They furnish, however, a considerable tonnage of very pure zinc.

355. Preliminary treatment. In a few favored districts in the United States there occur ores of such high grade that they can be treated directly. The bulk of our zinc, however, is derived from low-grade ores. Zinc ore, to be successfully treated by the present reduction processes, must contain at least 35 per cent of Zn and be relatively free from Pb, Fe, and Cd. The concentration process consists of crushing and grinding the ore to about 48 mesh and then subjecting it to gravity concentration or oil flotation in order to reject a large part of the gangue and undesirable minerals. The Huff electrostatic process and certain magnetic processes have found some application in the treatment of the more complex ores. The development of the electrolytic process has made available many complex ores which were formerly considered worthless. Ores with high percentages of Pb, Fe, and Cd could not be treated by the distillation process, but by careful treatment they are made amenable to leaching and electrolysis.

EXTRACTION OF ZINC FROM ITS ORES

356. General. Formerly zinc was universally extracted from its ores by distillation. Briefly, this consists in roasting the sulphide ore until the last trace of S is driven off and the sulphide is almost wholly converted into ZnO. If carbonate or oxide ores are used, it is necessary only to calcine them in order to drive off the water. This ZnO is then charged into a fire-clay retort along with carbonaceous material, such as anthracite or coke breeze, and heated to a temperature of about 1100° C. in a suitable furnace. Under such conditions the ZnO is almost completely reduced to metallic zinc, and this, at the high temperature of the retort, distills over and is caught in a fire-clay condenser attached to the mouth of the retort. Sphalerite (ZnS) is one of the most difficult of the metallic sulphides to

roast, and since we must obtain as nearly a dead roast as possible, the operation requires a long time and considerable fuel. The actual retorting consumes even larger quantities of fuel. As a result the reduction of zinc ores by distillation is one of our most wasteful metallurgical processes and is possible only where cheap fuel or natural gas is available.

The World War brought with it a demand for very pure zinc for the brass used in cartridge cases. As already noted, small quantities of impurities impair the malleability of brass, and these impurities are always present in all but the highest grade of zinc. This, together with the demand for a more economical process, gave impetus to research, and the present electrolytic process for reducing zinc was developed. This process consists, briefly, of roasting the finely ground sulphide ore to a mixture of ZnO and $ZnSO_4$. The roasted ore is then agitated with a dilute solution of H_2SO_4 and the zinc brought into solution. By filtration the solution is separated from the worthless gangue, purified, and electrolyzed. Under proper conditions the zinc is obtained in a very pure form, although not so cheaply as it can be smelted with natural gas or cheap coal. But it is generally conceded that the smelter has had its day. The zinc of the future will be produced by the electrolytic process or some modification of it.

CALCINING AND ROASTING

357. Calcining. The oxide ores are calcined before retorting in order to drive off the CO_2 and H_2O. If these are not eliminated they must be expelled in the retort, and this would be more expensive than roasting. Furthermore, the raw ore would take up more room in the retort. Carbon dioxide would tend to oxidize the Zn vapor in the retort or else consume excessive quantities of reducing agent. The zinc minerals give up their CO_2 and H_2O at about 400° C., and in so doing lose from 20 to 30 per cent in weight.

The furnaces for the calcination of oxide zinc ores are simple kilns (continuous shaft furnaces). The ore and fuel are charged in at the top in alternate layers. Air is admitted at the bottom, and as the charge sinks, with the combustion of the fuel and the withdrawal of calcined material below, more ore and fuel are

added above and the furnace is kept full. From 4 to 10 per cent of fuel by weight is used. The ore, in its passage down the shaft of the furnace, is heated to a high temperature and all the CO_2 and H_2O are driven off. The ore must not be finer than $\frac{1}{4}$ inch in diameter; otherwise it will tend to clog the furnace. A furnace 10 feet in diameter by 20 feet in height will treat about 40 tons of raw ore per twenty-four hours. Fine ores must be calcined in reverberatory furnaces.

358. Roasting blende. The object in roasting blende is to expel the S as completely as possible and to convert the ZnS into ZnO. As already pointed out under the discussion of roasting in general, sphalerite is one of the most difficult sulphides to roast; even under the best conditions the calcine will contain from 0.5 to 2 per cent of S, and under poor roasting conditions as high as 5 per cent. This ZnS is not reduced in the subsequent retorting, and all zinc thus combined goes into the residue and is lost. It is commonly estimated that each per cent of S will hold back 2 per cent of Zn.

Some sulphides can be readily roasted in a lump form, but blende cannot be so treated. It must be crushed to about 6-mesh size and then slowly and carefully roasted with frequent stirring. If the temperature is too low, $ZnSO_4$ will remain undecomposed; whereas if too high a temperature is reached, the associated sulphides will fuse, coat over the blende particles, and prevent complete roasting. Owing to these difficulties it is seldom possible to obtain a dead roast, and an ore is considered finished when the S has been taken down to 1 per cent. The ignition temperature of 100-mesh blende containing 0.30 per cent of Fe is 647° C., and of 50-mesh blende, 810° C. In general, the ignition temperature can be said to lie between 550° C. and 600° C. On the whole, blende roasts slowly; it does not swell and become porous as do most other sulphides; hence the air for oxidation cannot as easily reach the interior of the particle. If one is roasting for distillation, it is necessary to rabble the ignited blende frequently and to have, toward the end of the roasting period, a temperature of from 800° to 850° C. in order to decompose completely the $ZnSO_4$ that has been formed in the earlier stages. If there is iron present, zinc ferrite ($ZnO \cdot Fe_2O_3$) is formed. This compound is not reduced in subsequent distillation.

ROASTING FURNACES

359. General. Since roasted blende, for either the retorting or the distillation process, should contain as little S as possible, roasting in heaps, stalls, kilns, or coarse-ore furnaces is out of the question. Today all blende is roasted in some type of reverberatory or muffle furnace. The hand-raked reverberatory furnaces, while doing excellent work, are so costly in labor that they have been largely replaced by mechanically operated furnaces. The hand-raked reverberatory enjoys the advantage of close control of the operation. The ore can be moved rapidly through the cool part of the furnace, where it gives up its water and volatile constituents, and can then be held for a considerable period in the hottest part, near the fire bridge. Here the last of the S may be driven off. In the mechanically operated furnace the rate of passage of the ore must be constant. It requires two men to operate a 40×10 foot reverberatory which treats only about 3 tons of blende in twenty-four hours. Two men can operate several Wedge furnaces, treating, let us say, 200 tons of blende per twenty-four hours. For the purpose of this text only the Wedge and Hegeler furnaces will be described, since these are standard in American practice.

360. The Hegeler furnace. This furnace represents a type rather than an individual furnace, for the original design has been modified many times to suit local conditions. The furnace in use at one of the Eastern works is illustrated in Fig. 113. It consists of a rectangular brick block, 80 feet long, 17 feet wide, and 22 feet high, divided by a vertical partition into two separate compartments, or furnaces. Each compartment has seven arched hearths, 6 feet wide, lined throughout with refractory brick. As indicated in the vertical section, the lower three hearths are heated by muffles, and the upper four are heated simply by radiation and the heat of combustion of the ore. The heat for the muffles is supplied by gas which enters the heat flue (first gas), meets there air under a slight pressure, and burns with a long flame. This flame travels along underneath the bottom hearth to the opposite end, where it rises through a side pass to the next heating flue (second gas). Here it travels in the opposite direction, rises through a side pass to the next heating flue (third gas), and finally leaves through the waste-heat

flue. The heating flues as well as the side passes are sealed from the roasting compartment, so that the products of combustion cannot possibly mingle with and dilute the roaster gases.

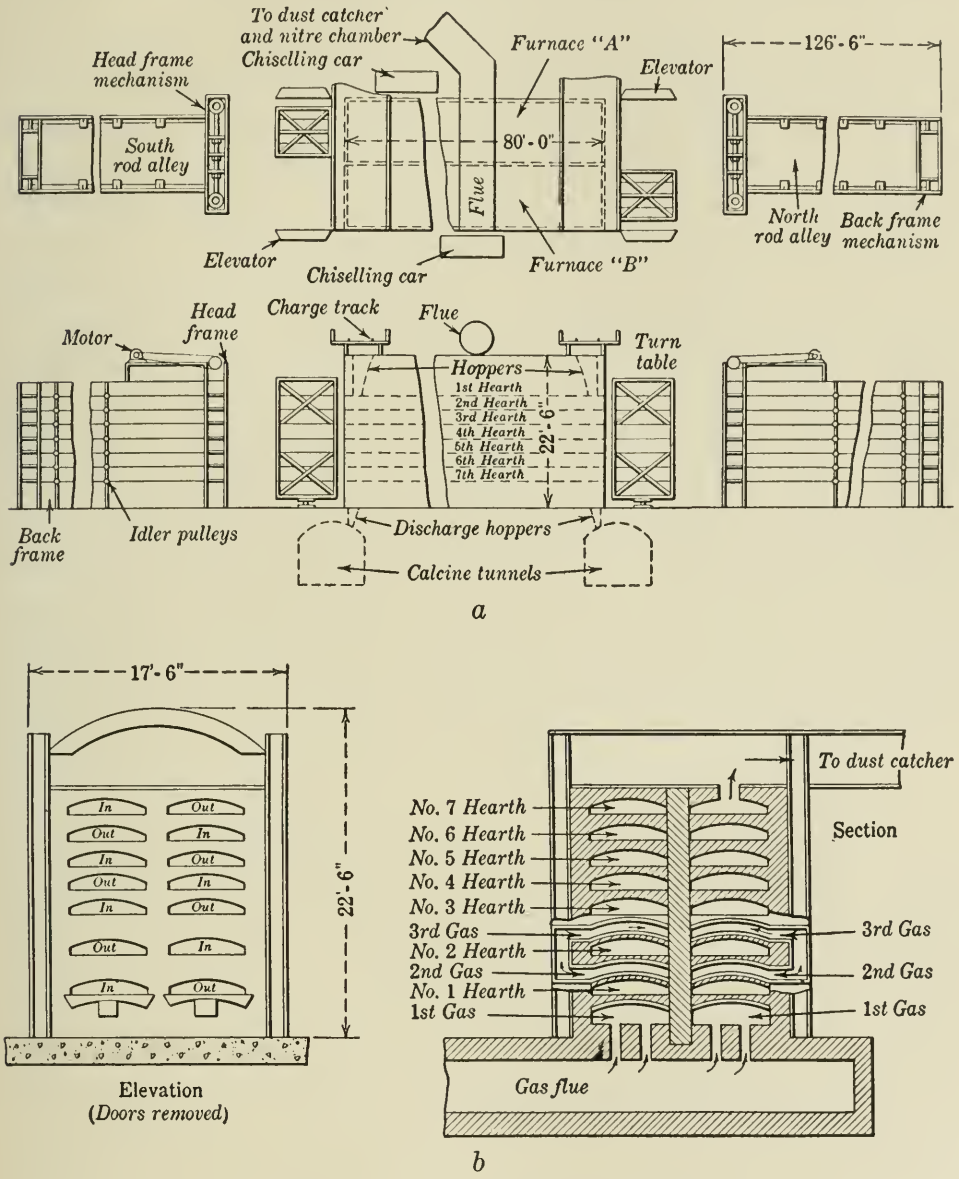

FIG. 113. The Hegeler furnace

The waste-gas flue conducts the hot gases into an air-heater of the pipe-stove type, which serves to heat the air for the bottom roasting hearth, thereby increasing the speed and the completeness of roasting. At some plants the gases are led directly to the air.

The raw ore, crushed to about 8-mesh size, is fed onto the top hearth of the furnace from a charging track and hopper, as indicated in Fig. 113, *a*. No. 1 compartment is fed at the opposite end from No. 2, in order that the same rake bar may be used for both compartments. The furnace has at either end a seven-stage turntable and a rod alley about 130 feet long. The open ends of all hearths are closed by means of tilting doors. The rabble frame or rake for stirring the ore is illustrated in Fig. 114. It enters the furnace at one end and is pulled through to the other end by means of a steel drawing rod attached to a motor-driven sprocket chain. When it emerges at the other end it is allowed to cool. It is then turned by means of the turntable through 180°, so that it may be pulled back in the opposite direction on the upper hearth of the other compartment. The rabble frame resembles a sled, with two side bars as runners, and with four cross bars which serve to rabble the ore and move it along the hearth. The ore, after its passage across the hearth, falls through a drop hole onto hearth No. 2, where it is rabbled and moved along by another rabble frame which serves the No. 2 hearth of both compartments. This is turned by a similar turntable. Thus a seven-hearth furnace will require seven rabble frames and fourteen rake bars. These rake bars must be of sufficient length to extend from the turntable on one end, through the furnace, and to the end of the rod alley on the opposite end.

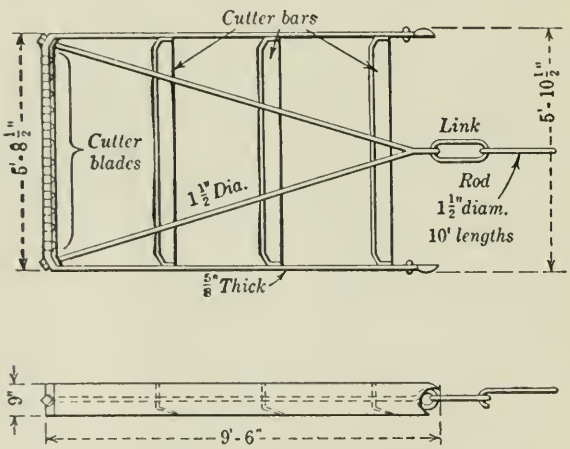

FIG. 114. A rabble frame

Such a furnace will roast 40 tons of dry ore per twenty-four hours from 24 per cent S down to 2 per cent S. With fairly free-burning ore the layer on the hearth will be about 4 inches deep. A furnace is raked about every two hours, and the ore will pass through a compartment in about thirty-six hours. A furnace will require the services of from two to five men and will consume about 1 ton of coal per ton of ore.

The roaster gases (containing about 4 per cent of SO_2) are withdrawn from the top hearth by a magnesite-lined kite flue, passed through a dust-catcher to enter the niter chamber of the sulphuric acid plant. At plants where the gases are not used for the manufacture of acid the S content of the calcines may be reduced lower than 2 per cent. At this particular plant the roasting operations have to be governed by the working of the acid chamber, as an attempt to dead-roast the ore would result in excessive dilution of the roaster gases.

361. The Wedge furnace. While the multiple-hearth Wedge furnace enjoys extensive use in the electrolytic-zinc industry, attempts to adapt it to the distillation process have apparently been none too successful. At one plant the floor of the fifth hearth of such a furnace was made thinner than usual in order to provide room for a muffle-like space between it and the roof of the sixth hearth. An outside fire box supplied heat to this muffle for roasting the ore after the S content had been reduced below the free-burning point. In this manner dilution of the roaster gases is avoided and the SO_2 content may be maintained around 6 per cent. Since the roasting operation is carried on at a much higher temperature than in ordinary sulphide roasting, special precautions have to be taken to avoid warping the arms.

DISTILLATION OF ZINC ORES

362. General. There has been but little change in this process since it was first developed. On the whole, it is one of the most wasteful, inefficient processes that we employ in the reduction of metals. Briefly, it consists in heating to a temperature of about 1300° C. a mixture of ZnO (roasted sulphide ore) and reducing fuel contained in fire-clay retorts. The ZnO is reduced to metallic zinc and the metal distilled off, much as alcohol is distilled from a fermented liquor. The zinc vapor is passed through a condenser in which it is collected as the liquid metal.

363. Chemistry. The reactions which occur in the distillation of roasted zinc ores are as follows:

$$ZnO + C = Zn + CO - 55{,}240 \text{ calories.} \quad (1)$$

$$CO_2 + C = 2\,CO - 36{,}880 \text{ calories.} \quad (2)$$

$$ZnO + CO = Zn + CO_2 - 16{,}360 \text{ calories.} \quad (3)$$

$$2\,ZnO + C = 2\,Zn + CO_2 - 71{,}600 \text{ calories.} \quad (4)$$

The charge in the retort usually contains from 40 to 60 per cent of the reducing agent, which is either anthracite or a mixture of this and coke breeze or bituminous coal. The reduction of ZnO by carbon begins just below the boiling point of zinc and is complete at about 1300° C. The CO formed in (1) reduces still more metal according to (3). Unless there is an excess of reducing agent over the amount theoretically required for the reduction of the ZnO, the CO_2 formed in (3) would reoxidize the zinc vapor with the formation of an excessive amount of blue powder. With a large excess of reducing agent the CO_2 is reduced to CO, which aids in the reduction of more ZnO. All the reactions are endothermic and require considerable heat in order that they may go to completion.

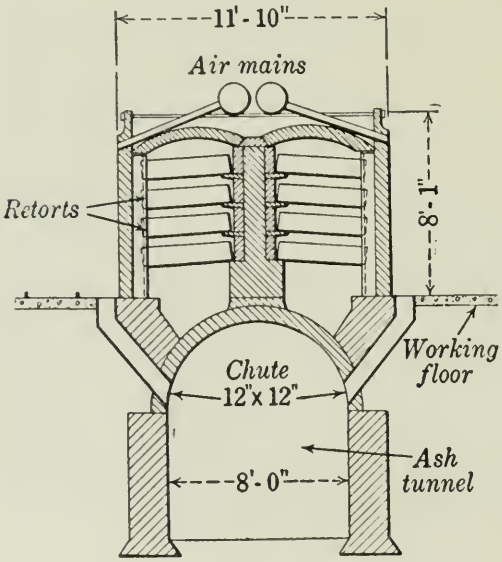

FIG. 115. The distillation furnace (section)

The reduction of ZnO is complete only at 1300° C. Zinc boils at a temperature of 907° C. The zinc thus reduced is in the form of a vapor which is carried away from the retort by the current of CO and condensed in the condenser. The temperature of the condenser is of the utmost importance, for if it is too high the vapor will of course fail to condense, and much metal will be lost. If, on the other hand, it is too low, say below the melting point of zinc (419° C.), the vapor will condense to blue powder, a mixture of ZnO and Zn.

364. The distillation furnace. The furnace in common use in the United States today is shown in Figs. 115 and 116. It consists of two units built back to back in order to reduce fuel consumption by cutting down the radiating surface. The retorts are cylinders of fire clay, from 48 to 54 inches long, 11 inches outside diameter, and closed at one end. The furnaces are built with from four to seven vertical rows of retorts, the former being the common type in this country. The retorts are supported in the furnace at a slight angle to the horizontal.

The back (closed) end of the retort rests on a shelf, or niche, built into the back wall of the furnace, while the front end rests on a cast-iron grill-work which forms the front of the furnace. The fire-clay condensers are inserted into the open end of the retort and the open space filled in with fire clay to prevent the loss of zinc vapor. Space between the sides of the retorts and the cast-iron grill-work of the furnace is filled with clay in a similar manner to prevent the loss of heat and to improve working conditions in front of the furnace, which at best are none too good. Furnaces are built with any number of retorts from 288 to 432 to a side. Large plants will have as high as 7000 retorts in operation.

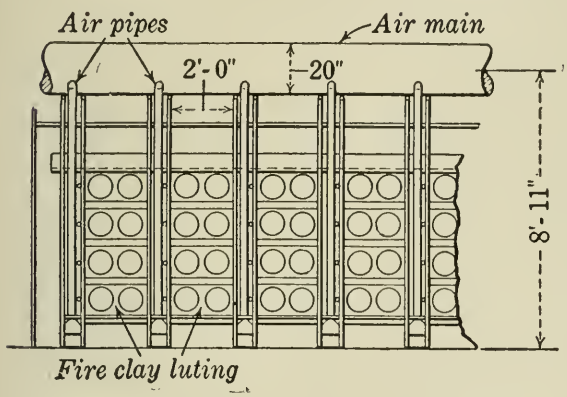

FIG. 116. The distillation furnace (elevation)

In the United States the furnaces are heated with either natural gas or producer gas. In Europe coal-fired furnaces are in use. The more intense heat and the flexibility of control with the gaseous fuel are obvious. In this country extensive deposits of natural gas offer a source of very cheap fuel, and our smelters are located with reference to these rather than to mines or zinc-consuming centers. The gas enters at one end of the furnace, meets air which enters through a number of small pipes inserted in the front of the furnace, and burns with a long flame. This flame is free to surround the retorts on all sides and bring them to a white heat. The waste gases leave the furnace at a high temperature, and consequently at many plants they are led into a checkerwork, or regenerative system, used to preheat the gas and air. Waste-heat boilers might be used, but a zinc smelter

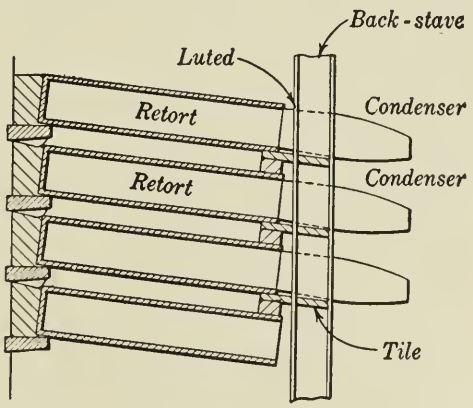

FIG. 117. The arrangement of retorts and condensers

consumes relatively small amounts of power, and such smelters are not located in districts where there is a ready sale for electrical power. The regenerative system is fast coming into common use, and it is estimated that it saves at least 50 per cent of the coal when producer gas is used.

Underneath the furnace is a tunnel through which the retort residues, broken retorts, condensers, and the general débris from furnace operations are removed. There are a number of inclined chutes between the working floor and this tunnel, one chute for every 18 to 24 retorts. The mouth of the chute is just in front of the furnace. These chutes discharge into cars which may be spotted on the track in the tunnel. When retorting is finished, the condensers are removed and the contents of the retort raked out onto the floor and shoveled into the chutes.

365. Retorts, condensers, and prolongs. The Belgian type of retort is used in the United States. This retort is a cylinder with a circular or elliptical cross section, open at one end and closed at the other. The extreme length of the retort varies from 36 to 60 inches, and the inner diameter, from 4 to 8 inches; the side wall is 1 inch thick, and the bottom, from $\frac{1}{2}$ to 2 inches thick. Such a retort will hold about 135 pounds of charge (0.9 to 1.7 cubic feet). Owing to the fact that the retorts must have considerable mechanical strength at the high temperature to which they are heated, and, further, that they must stand very rough usage, the best refractory material is none too good. The refractory should not soften at a temperature lower than 1710° C. and must be able to hold 150 pounds of charge at 1400° C. without sagging in the middle. The walls cannot be too thick, or the heat will penetrate the charge very slowly and unduly prolong the distillation period. The walls must be thick enough to be impermeable to zinc vapors. The retorts should not spall or crack when subjected to sudden fluctuations of temperature. A high-grade fire clay is the only material that will meet all these requirements. In the United States the fire clays used vary in composition between the following limits:

	Per Cent
Al_2O_3	23–38
SiO_2	59–46
H_2O	13–14
Bases	5–2

The life of a retort will depend upon the character of the ore and the temperature necessary for complete reduction. Ores that are high in lead or iron will slag the retort and thus weaken it. Fluctuations in the temperature cause it to crack or spall. Machine-made retorts last as long as forty days; hand-made retorts average about twenty days. Retorts in the hotter parts of a furnace last a shorter time than those in the cooler parts.

The condensers used vary considerably in shape. The length varies from 16 to 21 inches, the diameter at the larger end is from 6 to 7 inches, and the thickness of the wall is about $\frac{3}{4}$ inch. They should be of such a shape as to permit easy removal of the zinc when it has accumulated in the condenser, and yet they must not be so intricate as to make the cost of manufacture high. Condensers with a belly are more expensive to make than simple conical condensers, but hold much more zinc. They need not be of as refractory material as the retorts, since the load is small and they are not heated to as high a temperature.

Prolongs are sheet-iron tubes, from 2 to 3 feet in length, which are slipped on over the mouth of the condenser to collect any fume that may pass through it. They serve to collect the blue powder formed at the beginning of the distillation period. The recovery of zinc with prolongs will be about 3 per cent greater than with the simple condenser, and, furthermore, cadmium, which would otherwise pass off, is condensed along with the blue powder.

366. Manufacture of retorts and condensers. The material used in the manufacture of retorts and condensers consists of raw clay, burnt clay, quartzite, and limestone in proportions determined by the physical and chemical properties of the constituents. This mixture should be very refractory and yet have sufficient plasticity to be readily molded into shape. At some plants broken retorts are crushed and added, in small amounts, to the mixture. This mixture, whatever its composition, is crushed to 6 or 8 mesh. At some plants the material is bedded and crushed as a whole; at others each constituent is prepared separately. This mixture is fed into a pug mill along with from 16 to 20 per cent of water for hand work and from 10 to 14 per cent for machine-molded retorts. The tempered clay, in the form of balls or cylinders, is piled in heaps and allowed to weather from three to eight weeks and is then worked for a second time

before molding. Such seasoning materially improves the plasticity of the mixture. The preparation of the clay is very important; for the cost of retorts and condensers is a large item in the total cost of distillation, and their life depends more on the strength and durability of the clay than on anything else.

Retorts were formerly molded by hand, but on account of its high cost that method is now obsolete in this country. Several types of mechanically operated molding machines are in use. The most common one consists of a vertical plunger which may be forced into a cylinder of the same internal shape as the retort. A ball of clay, containing a little more than enough to form the retort, is placed in the cylinder. The piston in its ascent forces the clay out into the free space between the piston and the walls of the cylinder. A pressure of 3000 pounds per square inch compacts the mass so that it may be handled if some care is exercised. There is a device for allowing the entrained air to escape and for removing the retort after it has been formed.

The retorts, after molding, are placed in drying compartments, or rooms, each holding from 500 to 1500 retorts. They are piled on a lattice floor so as to allow a free circulation of the drying air. The rooms are heated by means of steam pipes placed under this floor, and the moisture is drawn off at the top. The retorts are moved from room to room as the drying process goes on. This drying should take place slowly. In the first room, where the temperature is about 30° C., they are kept for three weeks. The last room has a temperature of 70° C. The total drying time will average nine weeks.

The next step is the baking of the retorts. At some plants an attempt is made to cut down the loss of zinc vapor by painting the inside of the retorts with a mixture of low fusing point in order to glaze them over and effectually seal the pores. The object of baking is to drive off the last bit of chemically combined water and make them strong enough to be transferred from the baking chamber to the white-hot distillation furnace without damage. The baking oven is a brick chamber with a tile floor having openings spaced so as to leave room for the retorts to be placed on end between them. The hot gases from the fireplace ascend around the retorts and bring them to a constant heat. The temperature is brought slowly up to 800° C. and held there for twelve hours. They are not allowed to cool again.

As they are needed they are removed, while still red hot, and placed in the distillation furnace. Old retorts and condensers are freed from adhering slag, crushed to 8 mesh, and then used in the place of burnt clay in the retort mixture. Frequently the front end of condensers is separated from the rest, crushed, and treated on a concentrating machine to remove the metallic zinc.

367. Composition of the charge. The charges are made up of a mixture of calcined oxide ore or roasted sulphide ore and reducing fuel. It has been found best not to mix oxide ore with roasted sulphide ore, but to distill the two products separately. The reducing fuel will make up from 40 to 60 per cent of the charge by weight. A large excess over that theoretically necessary to reduce the ZnO is used in order to insure complete reduction and to maintain a reducing atmosphere in the retort by reducing any CO_2 that may be formed. The best reducing agent is anthracite crushed to about $\frac{1}{4}$ inch. This coal must be free from slate, pyrite, and other harmful impurities which might tend to slag the retort or combine with the zinc. Bituminous coal may be used to make up a part of the reducing charge; but if used alone, it makes too much gas, diluting the zinc vapor and causing the formation of an excessive amount of blue powder. It has the advantage, however, of depositing finely divided carbon, which is an active reducing agent. Coke is never used alone, for it requires a high temperature to be effective and does not deposit this finely divided carbon. Coke may make up as high as 25 per cent of the total reducing fuel.

If a smelter is treating both acid and basic ores it is well to treat them separately; otherwise they may slag in the retorts, film the particles of ZnO, and reduce the recovery of zinc. Ore and reducing fuel are crushed separately, the roasted blende to pass a 60-mesh screen, the reducing fuel to pass a 3-mesh or 4-mesh screen. The ore and fuel are fed into a rotary mixer and thoroughly mixed. Sometimes a little water is added, for it assists in more intimate mixing and enables the mixture to be more easily packed into the retorts. Since this mixture is voluminous and hard to handle, attempts have been made to briquette it before charging, but these have not been successful. Such briquetting would also increase the capacity of the furnace, since more ore could be introduced.

368. Apparatus and tools. The heat and fumes given off from the front of a furnace while it is in operation are such as to render the operations of charging, discharging, repairing, etc. decidedly uncomfortable. To protect the workmen as much as possible, use is made of the *Chapman shield*. It consists of two pairs of hinged sheet-iron curtains suspended from a traveling trolley. These are held apart by a spacer at the top and bottom so as to expose only three vertical lines of retorts, the rest being covered by the curtain. The curtain can be moved readily along the furnace by means of a sprocket chain. There is also a crane for holding a suspended pot for the collection of the molten zinc as it is ladled from the condensers.

Charging by hand is accomplished by means of a special scoop illustrated in Fig. 118. The ore mixture arrives in two-story charge cars and is removed with the scoop and thrown into the retorts. A skillful operator can pack a retort and spill but little ore in front of the furnace. It is very trying work, for the operator must do it in the face of the intense heat and the fume issuing from the retort. On the whole, it is slow, hard, and unhealthful work and requires considerable skill, and has therefore been given up in favor of mechanical charging.

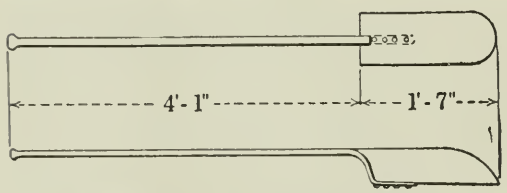

FIG. 118. A charging scoop

The Saeger charging machine is shown in Fig. 119. It consists of a lower truck *a*, an upper truck *b*, a charging hopper *c*, and a conveyor trough *s*. Truck *a* runs on tracks along the front of the furnace and carries truck *b*. The latter can be moved forward and backward on rails *e* by means of gearing. An electric motor to furnish power for the entire machine is mounted over truck *a*. In operation the motorman brings the machine into position in front of a set of retorts, moves forward the truck *b* until the conveyor troughs enter the mouths of the respective retorts, and starts the screw conveyors. While these are feeding, truck *b* continues to move forward until the screw conveyors have reached the end of the retorts, filling these part full. Truck *b* is then run backward, while the conveyors continue to feed until they leave the retorts. Hand charging of a certain furnace used to take 3 hours, but a Saeger charging ma-

chine does the work in 1 hour and charges 2000 pounds more than can be placed in the retorts by hand. Some care has to be exercised in charging materials that pack tightly, such as flotation concentrates, for gas is likely to accumulate in the back of the retort until the pressure is sufficient to blow out the whole charge.

369. Losses. The yield of zinc may reach 90 per cent, but the average in this country, owing to the fact that we must use impure ores, is probably nearer 85 per cent. The residue from retorting contains from 2 to 5 per cent of Zn. This zinc is present both as

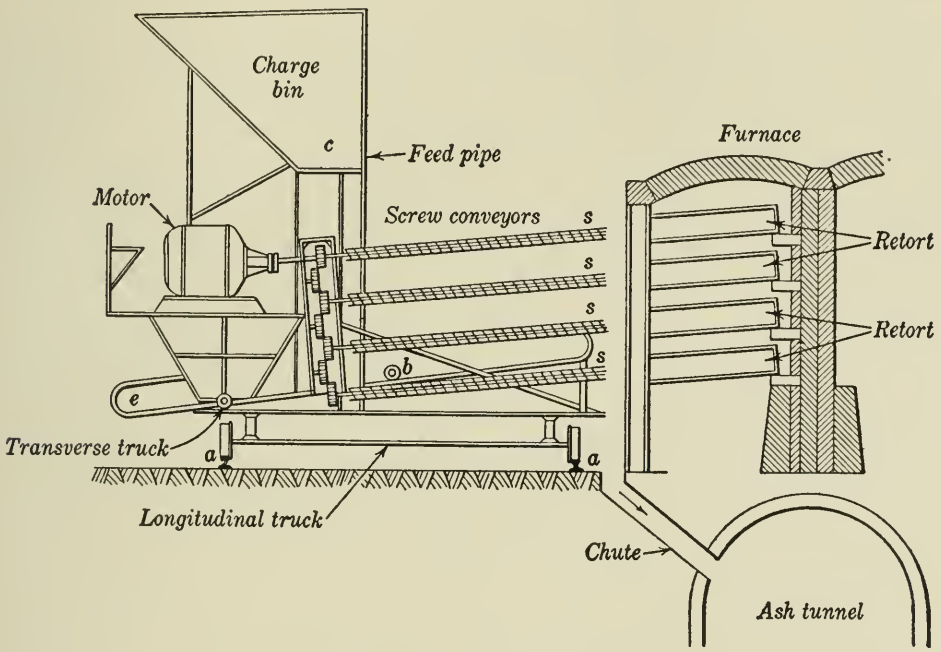

FIG. 119. The Saeger charging machine

undecomposed blende and as zinc ferrite, neither of which is reduced in the retort. The zinc ferrite is formed in treating ferruginous blende; it coats over the particles of ZnO and thus prevents their reduction. The retorts and condensers absorb metallic zinc and form a slag with ZnO. They are often permeable to zinc vapor and allow it to escape into the combustion chamber or into the open air. Broken or cracked retorts and condensers also cause a considerable loss of metal. The retorts frequently break at the beginning of the distillation period, and there is no easy way of recovering the charge for subsequent treatment. Zinc vapor, when the condensers are either too hot or too small, passes off into the open air and is lost. This loss is reduced somewhat by the use of prolongs.

370. Treatment of the residue. The residue left in the retorts after all the available Zn has been removed is called cinder. It consists of undecomposed ore, particles of slag and ferrite, and reducing fuel. The composition varies as follows:

	Per Cent
Zn	2–7
Pb	1–10
Fe	3–20
CaO, MgO	2–6
C	92–57

In treating ores containing precious metals all the Au and most of the Ag is left behind in this residue. In case the material contains enough Pb, Au, or Ag to warrant treatment, the residue is passed through a 6-mesh screen which removes most of the carbon and brings about a corresponding enrichment. The carbon may be used again with fresh reducing agent or it may be burned under the boilers of the plant. The undersize from the screen is then concentrated on tables, and this concentrate is added to the charge of a lead blast furnace. New methods involving volatilization are now being developed but as yet have not been applied commercially.

371. Operation of the furnace. Let us assume that the furnace has been started up and is in routine operation. The cycle of operations usually covers twenty-four hours. On arriving in the morning the day shift finds the furnace ready for cleaning, the last metal having been drawn off by the night crew and the temperature lowered considerably from the operating level. The shield is then brought along so that the operators may work on the first three rows of retorts, the adjacent ones being covered. A platform suspended from a trolley facilitates work on the upper retorts; the lower ones may be reached from the floor. With a special S-shaped tool the prolongs and condensers are removed and piled on end in front of the furnace. The residue close to the mouth of the retort is then removed and kept separate from the rest, since it is rich enough in zinc to warrant special treatment. The remainder of the residue is then raked out or blown out with compressed air and shoveled into the residue pockets. The operator examines all the retorts and, in case any are broken or defective, replaces them by others taken red-hot from the baking oven. When the retorts are filled by hand

this is done from the top down, one man shoveling to another standing on the platform, who charges the retort with a scoop. In large plants the work of discharging and charging is done by three crews, the first one removing the prolongs and condensers, the second cleaning out the retorts and replacing defective ones, while the third charges them with fresh material. In this way a bank of 240 retorts may be cleaned and charged by a crew of six men in four hours. Mechanical cleaning and charging takes about twenty-five seconds per retort.

The condensers are then luted into place, and the furnace is ready for distillation. The temperature is raised as quickly as possible, for during cleaning and charging it has been allowed to fall far below normal. Water vapor and light hydrocarbons are given off; these hydrocarbons are ignited and burn with a luminous flame. As the CO concentration increases, the flame changes to a purplish tint, finally assuming the bluish green of zinc vapor. As soon as the zinc begins to come off, the prolongs are attached to the condensers in order to catch the blue powder. Care must be exercised to keep the condenser at the proper heat, — from 415° to 550° C. If it is too cool, if there is CO_2 present in the retort, or if the zinc vapor is too dilute, an excessive amount of blue powder will be formed.

The first zinc comes off about six hours after charging has been finished. This zinc, as it collects in the condensers, is removed to a kettle. With average ores this dipping takes place about three times during the twenty-four hours. The dipping crew starts at one end of the furnace with a shield and pot. The zinc is ladled out into the kettle and covered with powdered charcoal or coke breeze to prevent oxidation. When the kettle is full it is removed and another is put in its place. The first kettle is drossed, to rid the zinc of oxide and impurities which have been mechanically carried over, and the zinc is cast into ingots ($9 \times 18 \times 1\frac{1}{4}$ inches), each weighing about 55 pounds. The dross is returned for redistillation. Very often the dippings are kept separate, for they vary considerably in composition. The metal first drawn off is the purest, since it is distilled at a comparatively low temperature. During the distillation period the temperature of the furnace must be kept above 1100° C., and toward the end of this period it must be held between 1300° and 1400° C. for a short time in order to bring off the last of the zinc.

REFINING CRUDE ZINC

372. General. The zinc obtained from the distillation furnace will contain from 96 to 98.5 per cent of Zn. The impurities are Pb, Fe, Cd, Cu, As, Sb, S, and Si. This crude material may be used for certain alloys, low-grade brass, and galvanizing, but for most industrial uses it must be refined. This may be accomplished by two methods: (1) redistillation and (2) liquation. Electrolytic refining has been tried; but while it produces a very pure zinc, the process is far more expensive than either of the other methods, and consequently is not practiced today.

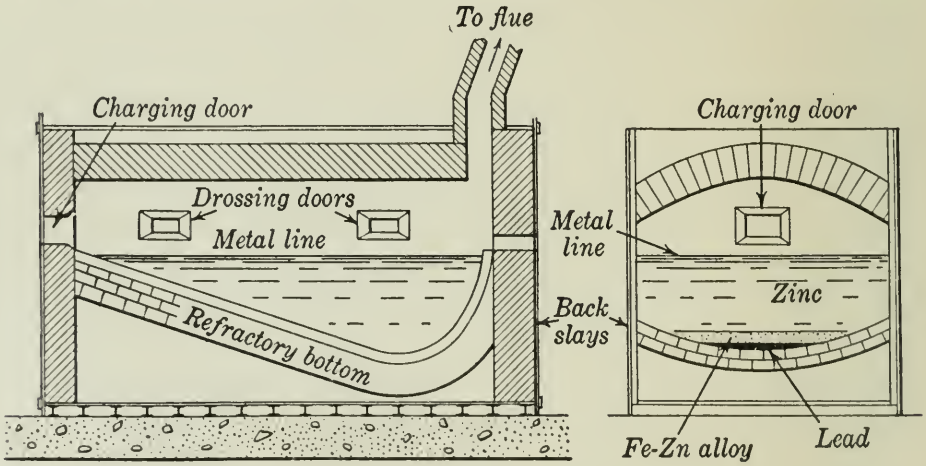

FIG. 120. A zinc liquation furnace

373. Liquation in a reverberatory furnace. A liquation furnace for the refining of crude spelter is shown in Fig. 120. The crude zinc is melted down in this furnace and kept at a temperature just above the melting point of the metal for from twenty-four to seventy-two hours. During this period oxides and non-alloying impurities rise to the surface as a dross. These are skimmed off from time to time and returned to the distillation furnace for re-treatment. Lead and a Zn-Fe alloy settle to the bottom of the furnace and collect in the cup-shaped depression at one end. The liquid lead thus collected contains about 45 per cent of Pb and is refined as already described under the chapter on lead. The Zn-Fe alloy contains about 6 per cent of Fe and is sold to the refiners of galvanizing scrap, who redistill it. At the close of the liquation period a part of the refined zinc is ladled out and cast into ingots, and a corresponding amount

of crude zinc is added to keep the bath at a constant level. When the accumulation of Pb and Zn-Fe alloy has risen to within 12 inches of the surface of the bath, charging is stopped and these accumulations are removed. The lead may be removed by lowering a pipe, plugged with a clay ball at the lower end, into the lead until it touches the bottom of the furnace. The clay ball can then be knocked off and the Pb ladled out. It may also be removed by means of an Archimedean screw in a cast-iron pipe. The mushy Zn-Fe alloy can be removed with a perforated ladle.

374. Redistillation. By this method a refined spelter with as high as 99.9 per cent of Zn may be obtained. Ordinarily consumers are not willing to pay the difference in cost between this and the fairly pure spelter obtained directly from pure ores, since it costs about 1 cent per pound for redistillation and there is a loss of about 5 per cent of the Zn in the process. In principle the process is the same as the distillation of ore, although, of course, the temperature need not be so high. The retorts, since they must hold a bath of molten metal, are level, not inclined, and the condensers are much larger. The furnace usually has three or four vertical lines of retorts. These are charged every twenty-four hours, and the metal is drawn off every four hours. Mechanically molded retorts last about sixty days. The following analyses show the degree of refinement accomplished:

	Crude Spelter	Refined Zinc
	Per Cent	*Per Cent*
Pb	1.5–3.0	0.10
Fe	0.3–1.01	0.01
Cd	0.03–0.07	0.03

ELECTROLYTIC ZINC

375. General. It has already been pointed out that commercial zinc or spelter is not nearly so pure as commercial lead or copper. Sometimes the impurities are not detrimental; at other times they seriously impair the valuable properties of the metal or alloy. For the manufacture of brass which is to be drawn or worked the zinc must be very pure. During the World War the demand for cartridge brass stimulated research and led to the development of the present electrolytic method for the reduction of zinc ores. By this means a very pure zinc can be prepared

from complex ores, but as yet this process cannot compete in cost with the older methods.

Briefly, the process is as follows: The finely ground sulphide ore is given an oxidizing roast so as to produce both oxide and sulphate of zinc. The former is readily soluble in dilute sulphuric acid; the latter in hot water. If the ore is a complex one, the lead and iron minerals are oxidized to sulphates and oxides, which are insoluble under the conditions of the leaching process. The roasted ore is then cooled and agitated for several hours with a dilute solution of H_2SO_4. The insoluble residue is then filtered off, the As, Sb, Cd, and Cu are precipitated, and the purified solution is electrolyzed with aluminum cathodes and lead anodes. By this means we are able to produce zinc of a very high degree of purity.

376. Roasting. The sulphide ore is crushed and ground until it will pass a 48-mesh screen. Fine crushing appears to be necessary in order to cut down the time of roasting and to expose the ore particles to the action of the leaching solution. The Wedge roaster is the machine almost universally used for this purpose. The object sought is the decomposition of ZnS into a mixture of $ZnSO_4$ and ZnO and the oxidation of the associated sulphides. The roast must be carefully carried out, for it has been found that a variable amount of water-soluble $ZnSO_4$ is necessary to replenish, by electrolysis, the sulphuric acid used up in the decomposition of the ore. Great care must be taken, particularly with complex ores containing Pb and Fe, not to attain too high a temperature in the roasting process. In the one case fusible compounds of lead form a coat over the ore particles and prevent oxidation; in the other case zinc ferrite (ZnO, Fe_2O_3) is formed, and the zinc thus combined cannot be dissolved in subsequent leaching. The roast therefore differs considerably from the roasting for distillation, where only ZnO is desired. Owing to the fact that $ZnSO_4$ is decomposed into ZnO and SO_3 at a temperature of 767° C., the temperature of the furnace must be kept below this point during most of the roast. Ordinarily it is not allowed to exceed 700° C., and with some easily roasted ores it may be held as low as 650° C. Contrast this with the 800°–850° C. required in roasting for distillation. It will be inferred from the statements above that one cannot hope to obtain a perfect roast, for although, if the tem-

perature is kept within these limits, the ore will be porous and there will be sufficient $ZnSO_4$, there will remain considerable undecomposed ZnS, particularly if the ore is relatively coarse.

A Wedge furnace 25 feet in outside diameter, with seven roasting hearths and one drying hearth, will roast from 40 to 50 tons of zinc concentrate in twenty-four hours from 25 per cent S down to 2 per cent S. After roasting, the material is cooled and stored in feed bins ready for the next step in the process, which is leaching.

377. Leaching. It will be noted in the complete flow sheet given in Fig. 121 that the leaching of the roasted ore is carried out in two stages, designated respectively as neutral leach and acid leach. This leaching is universally carried out in Pachuca tanks similar in principle to those used in the cyaniding of gold ores. Such a tank is illustrated in Fig. 126, p. 309. It differs slightly in constructional details, since it is called upon to handle a solution of a highly corrosive nature.

The solvent for the neutral leach is made up of cell acid (overflow of the electrolytic cells with from 10 to 20 per cent of H_2SO_4 and from 2 to 3 per cent of Zn) and of tailing solution of the acid leach (1 per cent of H_2SO_4 and 10 per cent of Zn). This pulp is agitated in a series of Pachuca tanks for several hours. The object of the neutral leach is to dissolve about 75 per cent of the Zn (most of which is water-soluble), neutralize the free acid, oxidize and precipitate the Fe and along with it most of the As and Sb dissolved from the ore, precipitate the Cu, and coagulate the gelatinous silica which would interfere with filtration later on. The As and Sb are precipitated as basic salts of iron. There must be enough Fe to cover this reaction. Sometimes it is necessary to add some in the form of $FeSO_4$. It is also necessary to add MnO_2 to insure complete oxidation of the iron. After agitation, the pulp is sent to a Dorr classifier or a similar classifying device, where it is separated into a sand and a slime. The latter is sent to a thickener, where it is separated into a clear overflow and a spigot. The spigot goes to the acid leach and the overflow to the purification tanks to be prepared for electrolysis. The former may be treated in two ways: it may be ground and sent directly to the acid leach, or it may be ground and treated by oil flotation to recover any undecomposed blende.

The object of the acid leach is to dissolve the last of the extractable zinc. The material treated consists of the spigot of the neutral thickener and ground sand from the acid leach. The solvent is cell acid (from 10 to 20 per cent of H_2SO_4 and from 2 to 3 per cent of Zn). The pulp is agitated in Pachuca tanks for from six to ten hours. During this time the Cu and all the extractable Zn are leached out, and the free acid is reduced to about 0.5 per cent. After agitation, the pulp is passed to Dorr thickeners and separated into a spigot and a clear overflow. The former, if it contains enough lead, may be smelted direct; otherwise it is a waste product. The latter goes to storage to make up solvent for the neutral leach. It has been found that the acid content should be held rather closely to 0.5 per cent H_2SO_4. If it is less than this, some Zn remains undissolved and the filter cake is high in moisture, owing to the presence of gelatinous iron and aluminum salts. If it is higher than 0.5 per cent H_2SO_4, the free acid hinders settling and unduly increases the amount of Fe in the electrolyte.

378. Purification. The clear solution from the neutral leach, besides about 6 per cent of Zn, contains Cu, Cd, and traces of As and Sb which have escaped precipitation in the neutral leach. The Cu and Cd are precipitated by agitation with zinc dust in Pachuca tanks. The allowable impurities in the solution to be electrolyzed are as follows:

	Milligrams per Liter
Cu	10
Mn	350
As	1
Sb	1
Fe	30
Cd	20
Co	1

After purification, which is usually complete in about thirty minutes, the contents of the tank are drawn off into a Dorr thickener. The spigot of this thickener is stored for future treatment, and the clear overflow goes to the electrolytic cells.

379. Electrolysis. This is carried out with lead anodes and sheet-aluminum cathodes. A slightly acid solution of $ZnSO_4$ is dissociated into Zn and SO_4 ions. In electrolysis the Zn ions migrate to the cathode, give up their charges, and are

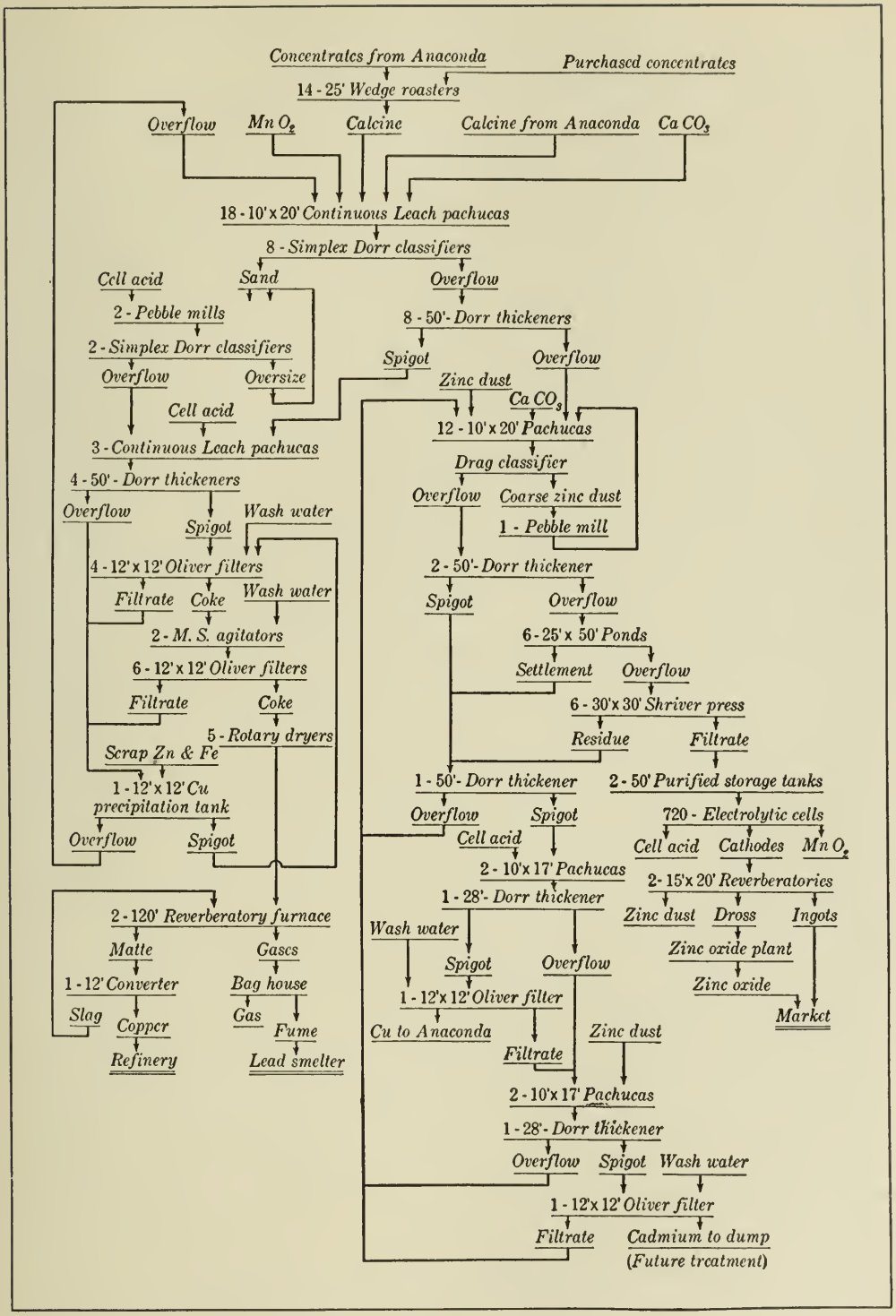

FIG. 121. Flow sheet of the Great Falls electrolytic plant

deposited as metallic zinc. The SO_4 ions move similarly to the anode, give up their charges, and form H_2SO_4 and O. The decomposition voltage of $ZnSO_4$ is 2.35; that of H_2SO_4 is 1.67. The working voltage of the tank is held at about 3.5. Theoretically 1.2194 grams of zinc per ampere hour should be deposited, but in practice about 1.5 kilowatt hours per pound of zinc is required. The principal factors which affect the character of the zinc deposit are temperature, current density, concentration of Zn and H_2SO_4 in the solution, and the presence of impurities.

A current density of from 20 to 25 amperes per square foot of cathode area and a temperature of from 40° to 50° C. is considered good practice in this country. One great trouble encountered is the formation of a soft, spongy deposit of zinc. It is almost impossible to melt this without a high loss, owing to its tendency to oxidize. In general it may be stated that a high current density favors a firm deposit, and that as the density is increased the temperature of the electrolyte must be lowered. High temperature increases corrosion and reduces the current efficiency. Often it is necessary to provide lead cooling coils in order to keep the temperature of the electrolyte within the above range.

The solution to be electrolyzed should be nearly neutral and should contain, on entering the electrolytic cells, about 10 per cent of Zn. On leaving, it will contain about 3.5 per cent of Zn and from 10 to 12 per cent of H_2SO_4. Since Zn is more electropositive than H, H_2SO_4 is decomposed before $ZnSO_4$, and Zn will come down only when there is an overvoltage of 0.77. Hence the higher the content of free acid the more H will be set free and the lower will be the current efficiency.

The solution for electrolysis must be carefully purified and all impurities electronegative to zinc eliminated; otherwise they are likely to lower the current efficiency and cause the formation of spongy zinc on the cathode. It is estimated that impure zinc is fifty times as soluble in dilute H_2SO_4 as pure zinc. In electrolysis, with sufficient impurity, re-solution might completely offset the depositing power of the current, with the result that no zinc would be deposited at all, but only H generated at the cathode and O at the anode. With smaller amounts of impurities this effect shows up as more or less marked corrosion of the cathode and a reduction in the current efficiency. Cu and

Cd affect the character of the deposit, eating holes in the cathodes and leaving a black deposit on the aluminum sheet. Fe, As, and Sb are not precipitated but reduce the current efficiency. Mn is relatively harmless, but with low acid content MnO_2 adheres to the anode and has to be scraped off. The alkali metals and Mg have no bearing on the process. Compounds of Cl must be absent, for the Cl liberated in electrolysis attacks the lead anode. A foul solution may be improved by adding from 0.5 to 1.5 ounces of glue per ton of metal; in extreme cases a part of the solution may be drawn off and purified as in the refining of copper. It has been found far better, however, to take more care with the initial purification.

380. Tanks. The multiple system is used in this process, the tanks being arranged in cascade as in the electrolysis of copper. A cell is 10 feet long, 2 feet 10 inches wide, and 5 feet deep, made of 4-inch planking lined with sheet lead. Each cell has 28 anodes and 27 cathodes. The anodes are cast lead, the cathodes are sheet aluminum. Each cathode is 2 feet wide, 3 feet 6 inches long, and $\frac{3}{16}$ inch thick, while the anodes are slightly smaller. Wooden strips are attached to the sides of the cathode sheets to prevent "sprouting" and to facilitate the removal of the deposited metal. The electrode distance is $1\frac{3}{4}$ inches. The cathodes are stripped every forty-eight hours, a sheet so stripped weighing from 15 to 22 pounds. Anodes are cleaned every four to six weeks.

381. Melting cathodes. Cathode sheets cannot be marketed as such but must be melted down and cast into bars. There is a considerable loss (from 4 to 5 per cent of the zinc) in this step, owing to oxidation of the zinc, to porous sheets, and to the presence of $ZnSO_4$. The dross formed contains from 40 to 50 per cent of metallic zinc. A part of this is recovered by liquation with NH_4Cl, while the remainder is worked up into zinc oxide.

382. Plants. Each ore presents a problem in itself, so that no general flow sheet can be made covering all ores. The presence of Fe, As, Sb, or Ag and the ease of roasting, leaching, or filtration profoundly affect the scheme of treatment. Fig. 121 gives, in diagrammatic form, the flow sheet of the Great Falls plant of the Anaconda Copper Mining Company. The ore treated is a flotation concentrate containing from 33 to 35 per cent of Zn, about 1.5 per cent of Cu, 9 per cent of Pb, and 12 per cent of Fe.

THE SUNNYSIDE CONCENTRATOR

383. Ore. This plant of the United States Smelting, Refining, and Mining Company has a capacity of about 750 tons per day. It is engaged in treating a complex ore consisting of a mixture of galena, sphalerite, and pyrite in a gangue of quartz and rhodonite. The mill feed averages as follows:

Pb	From 4.5 to 5.0 per cent
Zn	From 6.5 to 7.5 per cent
Fe	From 3.5 to 4.5 per cent
Cu	From 0.4 to 0.6 per cent
Ag	From 3.0 to 4.0 ounces per ton
Au	From 0.04 to 0.10 ounce per ton

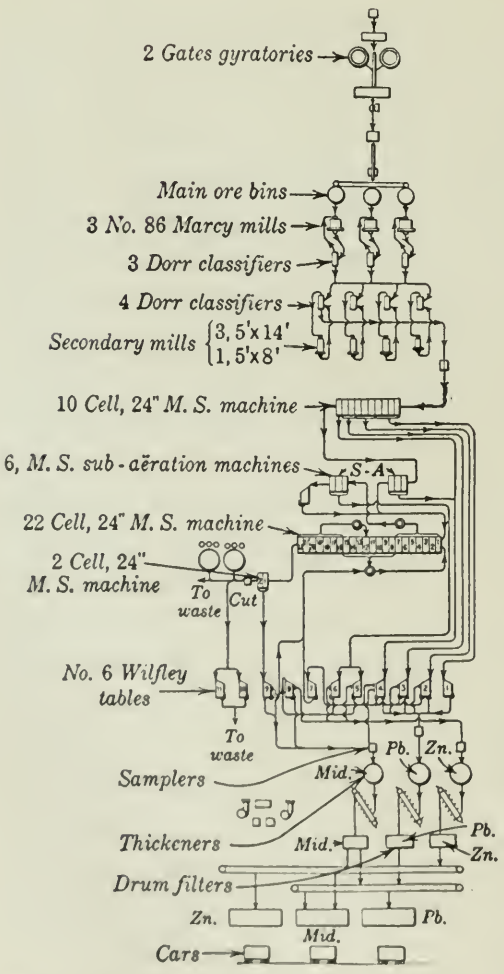

FIG. 122. A flow sheet of the Sunnyside concentrator

Before the development of selective flotation an ore of this type could not be successfully concentrated, owing to the fine character of the ore minerals. Even now much remains to be done, for in order to meet smelter schedules it is often necessary to sacrifice recovery and keep concentrates up to grade.

384. Crushing and grinding. The flow sheet of the plant is given in Fig. 122. All ore is weighed by a weightometer before going to the main ore bins, which have a capacity of 1300 tons. This ore has been crushed in gyratories at the mine to pass a $2\frac{1}{2}$-inch grizzly. It is then fed into three No. 86 Marcy mills working in closed circuit with Dorr classifiers. Certain flotation oils are added to the classifier return. The pulp then

passes to the tube-mill circuit, which consists of three 5 × 14 foot pebble mills and a 5 × 8 foot ball mill. These also work in closed circuit with a Dorr classifier. The overflow of these classifiers is maintained at about 26 per cent solids, all minus 65 mesh, and about 60 per cent minus 200 mesh. Contrast this fine crushing with the relatively coarse and graded crushing employed in the Hecla mill (see pages 241–246). At this plant, owing to the fine state of division of the mineral particles, it is virtually impossible to make a concentrate on the coarse sizes. At the Hecla plant it is not only possible but, owing to subsequent smelter treatment, very desirable to do so.

385. Oil flotation. The pulp from the secondary mills forms the feed of the flotation department. Lead flotation is carried out in a 10-cell, 24-inch Minerals Separation machine. The concentrates from the first four cells form a finished lead concentrate. Those from the other six cells are tabled, forming a finished lead concentrate, middlings, and tailings, the disposal of which will be discussed later. The tailings from the lead cells pass to a group of three subaëration cells, the concentrates from which are tabled to give a finished lead concentrate, middling, and re-treatment products. Tailings from the group of three secondary lead cells form the entire primary feed to the zinc-flotation cells. All zinc concentrates are re-treated at least once by flotation, and all final zinc concentrates are tabled.

386. Dewatering. Three Dorr thickeners are employed for thickening the lead concentrates, zinc concentrates, and middlings. The underflow from each thickener is elevated to a Portland filter, from which the cake is transferred by a belt conveyor to the shipping bins. The lead cake contains about 6 to 8 per cent moisture; the zinc, from 6 to 7 per cent; and the middling, about 5.5 per cent. The 750 tons of mill feed yield about 60 tons of lead concentrates, 65 tons of zinc concentrates, and 15 tons of a mixed lead-zinc concentrate (middling). The lead concentrate and middling go to a lead smelter at Durango, and the zinc concentrate to a zinc smelter in Oklahoma for reduction. Table XXXIX indicates the analyses of the different products and the respective recoveries obtained. Generally speaking, the aim is to get a high recovery in the lead concentrate and middling, and a high grade in the zinc concentrate.

TABLE XXXIX. AVERAGE ANALYSES AND RECOVERIES (SUNNYSIDE)

	ANALYSES					RECOVERIES				
	Au	Ag	Pb	Cu	Zn	Au	Ag	Pb	Cu	Zn
	Ounces per Ton	*Ounces per Ton*	*Per Cent*	*Per Cent*	*Per Cent*	*Per Cent*	*Per Cent*	*Per Cent*	*Per Cent*	*Per Cent*
Mill feed . . .	0.072	3.66	4.8	0.49	7.2	—	—	—	—	—
Lead concentrate	0.54	25.0	46.7	2.84	12.9	54.8	49.5	70.9	41.7	12.9
Zinc concentrate	0.08	6.8	5.7	1.17	53.8	9.9	16.3	10.6	21.0	66.0
Middling . . .	0.34	16.3	15.4	3.2	26.5	11.1	10.6	7.6	15.4	8.7
Tailing	0.02	1.06	0.63	0.13	1.1	24.2	23.6	10.9	21.9	12.4

387. Flotation reagents. It has been found necessary to employ a large number of flotation reagents. For floating the lead, coal tar, hard-wood creosote, crude naphthalene, and sodium sulphite are added to the primary ball mills. Then to the agitating compartment of the first lead cell is added more of the reagents mentioned above, together with soda ash, pine oil, potassium xanthate, and sodium silicate. The total amount of reagents added to the lead circuit is about as follows:

	POUNDS PER TON OF ORE
Coal tar	0.15
Hard-wood creosote	0.05
Soda ash (58 per cent)	1.00
Xanthate	0.05
Sodium sulphite (crystals)	0.25
Sodium silicate	0.75
Naphthalene	Trace

To the first cell of the zinc-flotation roughers is added a mixture of copper sulphate, xanthate, hard-wood creosote, coal tar, and pine oil. More copper sulphate is added to the first of the three subaëration, zinc-cleaner cells treating the concentrate from the seven zinc rougher cells. The total amount added to the zinc circuit is about as follows:

	POUNDS PER TON OF ORE
Coal tar	0.08
Hard-wood creosote	0.04
Pine oil	0.05
Copper sulphate (crystals)	1.5
Xanthate	0.18

388. Indicator tables. The tables are used largely as indicators to check up the work of the flotation machines. The single table used in connection with the subaëration machines is purely an

indicator, its entire product going back to the zinc roughers. Table No. 1, of the group of eleven tables following lead flotation, is used as an indicator of zinc and iron in the lead concentrate from the first four cells. If too much is visible, the need of adjustment of the oils or sodium silicate is indicated. If too much zinc is seen, more sodium sulphite is advisable. No separation of any kind is attempted on this table, the whole product being finished lead concentrate. Tables Nos. 2, 3, and 4 serve, to a certain extent, as indicators, but they also make a middling and tailing, which are either shipped as middlings or go back to the lead cells for re-treatment. Tables Nos. 5 and 6 are fed with the zinc-cleaner concentrates. These come off the table largely as a slime and go directly to the dewatering department for shipment. They indicate excessive amounts of lead and iron in this product. If there is too much lead present, the machines are adjusted or more oil is added to the lead circuit. If there is too much iron present, the oils or copper sulphate are reduced. Table No. 8, besides serving as an indicator, is used to split a return to the zinc circuit and a middling shipping product. Table No. 9 is used for splitting the concentrate from the two scavenger flotation cells into the most economical products. Tables Nos. 10 and 11 are used solely as indicators taking a cut from the mill tailing. If lead or zinc appears, while no attempt is made to recover it, steps are immediately taken, by a change in the adjustment of the machines or of the oil mixture, to prevent its coming through.

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CHAPTER X

GOLD

389. Physical properties. Gold is the most malleable and ductile of all our metals. For example, it is possible to make gold leaf which is less than 1/300,000 of an inch in thickness, and wire may be drawn so fine that 500 feet of it weighs only 0.06 gram. The yellow color of gold may be modified by the presence of other metals, such as silver, nickel, and iron. It is softer than silver but harder than tin. Its specific gravity varies from 19.29 to 19.37, according to whether the metal has been cast or rolled. Its tensile strength is about 14,000 pounds per square inch. The melting point of gold is 1063° C. It begins to volatilize at 1100° C., but up to 1300° C. losses from this cause can be neglected in the operation of industrial furnaces. Its electrical conductivity is 76.7 as against 100 for silver.

390. Chemical properties. The common solvents of gold are aqua regia, solutions of chlorine, and solutions of cyanide. It is not perceptibly attacked by alkalies, and H_2SO_4, HNO_3, and HCl, separately, have little action on the metal. Many impurities, even when present in small amounts, have a decided effect on the properties of the metal. For example, minute quantities of Pb, Bi, Cd, Sb, As, and Sn produce brittleness. As little as 0.05 per cent of Bi makes gold so brittle that it can be crumbled between the fingers. Gold will alloy with most metals, but the only ones of importance in industry are alloys with Ag, Pt, Hg, and Cu. Gold unites with Hg to form a white, solid amalgam containing about 32 per cent of Au.

Jeweler's gold ranging from 18 (750 fine) to 10 carat (416 fine) also contains Ag and Cu. The lower grades contain notable percentages of Zn. White gold is properly an alloy of gold and palladium (75 per cent of Au, 25 per cent of Pd). A cheap imitation of white gold is produced by alloying gold with nickel. Green gold contains Cu and Zn. Aluminum forms a number of alloys with gold, one of these (22 per cent Al) having a beautiful purple color.

TABLE XL. WORLD'S PRODUCTION OF GOLD*

	1910	1915	1920	1925
	Fine Ounces	*Fine Ounces*	*Fine Ounces*	*Fine Ounces*
United States	4,657,017	4,887,604	2,476,166	2,319,920
Canada	493,707	916,076	766,913	1,735,735
Mexico	1,205,051	317,305	738,472	788,993
Brazil	94,557	117,286	87,075	108,506
Russia	1,721,163	1,382,867	70,000	1,060,950
Congo	†	49,787	96,804	122,781
Transvaal	7,534,120	9,096,106	8,158,455	9,597,592
India	518,502	557,399	436,719	393,807
Australasia	3,167,140	2,389,619	1,144,024	673,119
All others	2,605,040	2,044,759	2,230,401	2,258,512
Total	21,996,297	21,758,808	16,205,029	19,059,915

† Not available.

TABLE XLI. PERCENTAGES BY WEIGHT OF GOLD FROM VARIOUS SOURCES IN THE UNITED STATES

	1910	1915	1920	1925
Placers	23.76	22.66	25.30	18.91
Siliceous ores	68.91	67.57	63.93	61.30
Copper ores	5.77	7.22	7.18	15.08
Lead ores	1.18	1.78	1.96	2.18
Zinc ores	0.07	0.10	0.15	0.02
Complex ores	0.31	0.67	1.48	2.51

391. Ores. Gold is very widely distributed in nature in both the native and the combined form. Native gold occurs as grains or particles disseminated through veins of quartz and other rocks. It frequently occurs, in small quantities, in various ores of lead, copper, and, less frequently, zinc. The source of our domestic gold is indicated in Table XLI and the world's production of gold in Table XL. When gold ores are broken up by weathering and disintegration, the gold is freed, and since it is not attacked by ordinary solvents, it is concentrated by the streams and rivers into deposits of placer gold, often of considerable extent and value. It was gold of this description that first attracted the "Argonauts" to California and opened up our West. This vein and placer gold varies in purity from 500 to 950 parts per 1000 parts of alloy. In size it ranges from minute flakes, so small that they will scarcely settle in water, up to

* Annual Reports, Director of the Mint.

masses, or nuggets, of 2000 ounces or more in weight. Gold very frequently occurs along with silver and such minerals as galena, chalcocite, chalcopyrite, and pyrite. The only gold minerals so far discovered are the tellurides calaverite ($AuTe_2$) and sylvanite ($Au, AgTe_2$). Sometimes an ore may be mined for its gold content alone. When this is done the value of the ore will depend upon its chemical composition and its nearness to transportation. Some relatively high-grade gold ores cannot be made to yield a profit today, owing to their complex nature. At the Homestake mine in North Dakota an ore with only $1.75 per ton in gold is being treated at a profit, while in districts remote from cheap transportation ores containing as much as $50 per ton would not yield a profit. More often the gold is obtained as a by-product in the smelting and refining of copper and lead ores. Smelters, in buying such ores, usually pay for the gold when it is over 0.025 ounce per ton, and for silver when it is over 1 ounce per ton. Placer deposits that contain only 6 cents in gold per ton, or, roughly, 1 part in 10,000,000, are being worked by dredging methods.

It has long been known that sea water contains small amounts of gold and silver. The average amount is about $\frac{1}{40}$ grain, or 0.1 cent per ton. The ocean contains 320,000,000 cubic miles of water, each containing 4,600,000,000 tons, so that the aggregate amount is truly enormous. The cost of recovering such small percentages would likewise be enormous. Nevertheless many projects, usually of a shady nature, have been launched to do this.

The amount of gold in an ore or metallurgical product is usually expressed as so many ounces per ton, grams per ton, or dollars per ton. If it is in the form of bullion, it is expressed in fineness; that is, a bar of bullion is said to be 850 fine when it contains 850 parts of Au per 1000 parts of bullion. In England and her colonies ores are valued in pennyweights of gold per ton or in shillings per ton. The United States coins are 900 fine. The mint value of gold is $20.67 per ounce.

392. Extraction of gold from its ores. Gold may be extracted from placer deposits by the simple process of gravity concentration. Gold chemically combined or very finely disseminated through an ore cannot be as easily recovered. Many complex ores are waiting for some cheap, efficient process to make their

treatment worth while. Gold usually occurs with silver, but in those ores in which it is the principal metal the gold may be recovered by the following processes: (1) amalgamation; (2) chlorination; (3) cyanidation; (4) combinations of amalgamation, gravity concentration, oil flotation, and cyanidation.

CRUSHING OF GOLD ORES

393. General. Before the ore can be treated by any of these processes, it must be crushed and ground to a very fine state of division in order to free the gold particles for concentration or to expose them to the action of some solvent. Some ores crushed to pass a 10-mesh screen are fine enough, while other finely disseminated ores or those of a more refractory nature must be slimed, or ground, to pass a 200-mesh screen. The crushing may be carried out in gyratory, or Blake, crushers, followed by disk crushers, ball mills, or tube mills. There is one machine which was originally developed for the crushing of very hard gold-quartz ores, and this one still enjoys considerable popularity in spite of the developments which have been made in ball-mill and tube-mill grinding. This machine is the California stamp mill.

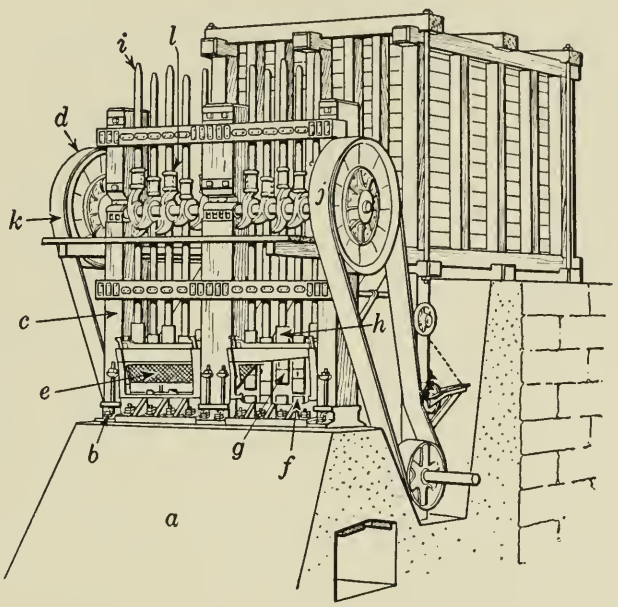


FIG. 123. A California stamp mill

394. The stamp mill. A complete stamp mill is shown in Fig. 123. The principal parts are designated by letters: *a*, the concrete mortar block, or foundation, carrying the weight of the entire mill; *b*, the cast-iron mortar box, or mortar, in which the ore is crushed; *c*, the stamp frame of heavy timbers; *d*, the bull wheel for driving the stamps; *e*, a punched plate or woven-wire screen; *f*, the dies which receive the blow from the falling

stamp; *g*, the shoe; *h*, the boss head; *i*, the stamp stem; *j*, the cams, which are firmly keyed to the horizontal shaft; *l*, the tappets by which the stamps are raised.

In operation the ore, with about six times its weight of water, is fed into the mortar at a uniform rate. This constant rate is very essential; for if the ore is fed too slowly, there is excessive wear of the dies and shoes, and if it is fed too fast, the battery does not operate efficiently and the pressure of the ore and water may even destroy the screens. The stamp mill does not work efficiently as a primary breaker; so the ore must first be crushed, by means of gyratory, or Blake, breakers, to about 2 inches diameter or preferably smaller. The horizontal shaft of the stamp mill is revolved by means of the bull wheel, so that the stamps will make about 100 drops per minute. The rate of drop will be governed entirely by the character of the ore and the height of the drop. The common order of drop is 1, 4, 2, 5, 3. The pieces of ore are caught between the falling stamp and the die and crushed. The complete stamp (stem, tappet, boss head, and shoe) will weigh from 500 to 2100 pounds, so that the crushing effect when this drops from a height of from 6 to 9 inches is considerable. The screen, fixed in the front of the mortar, determines the size to which the ore will be crushed before it is ejected. The mortar is lined — back, sides, and front — with plates of chrome or manganese steel to protect it from the wear and attrition of the ore. Between the mortar and the concrete foundation are inserted rubber sheets or woolen blankets to absorb some of the vibration set up by the operation of the stamp. At best this is terrific, and many of the parts, such as stamp stems, cams, etc., break through fatigue long before they are worn out. The shoes and dies are easily removed, so that as they become worn they may be replaced by others. The shoes and dies do not wear evenly, the center wearing away much faster than the edges. This diminishes the effectiveness of the crushing action, and owing to this distortion it is often necessary to replace shoes or dies long before they have been worn out. The tappet is adjustable, so that any height of drop may be obtained as the shoes and dies wear away. The stamp mill will do its best work when crushing to about 20 mesh. For very fine crushing (to 100 mesh or finer) it is best to use some other type of grinder.

AMALGAMATION

395. Preparation of ore. As has been pointed out, gold is easily soluble in mercury, and the alloy is termed an amalgam. Before such dissolving action can go on it is necessary to free the gold from the inclosing rock. This is usually done by means of the stamp mill or some type of ball mill. It may be necessary to crush the ore to from 30 to 100 mesh, according to the character of the ore.

396. The amalgamating table. This is set up immediately in front of the battery so as to receive the discharge of the mortar. The table should be independent of the battery frame in order to eliminate the vibration so far as possible. Its width will be about the length of the discharge opening in the mortar, and its length from 6 to 20 feet. The inclination of the plates will vary from $\frac{1}{2}$ inch to $2\frac{1}{2}$ inches per foot. It should not be so flat that coarse material will bank and thus cover the active surface, or so steep as to induce a scouring effect. The table is covered with pure copper plates, about $\frac{1}{8}$ inch in thickness, firmly secured to the table by means of wedges and cleats. The preparation of these plates is very important, for on the consistency of the amalgamating surface depends, to a large extent, the efficiency of the process.

The copper plates, made of metal as pure as possible, are first carefully annealed. They are then thoroughly cleaned of dirt and grease by means of sodium carbonate, emery, and sand so that the surface is bright and smooth. Mercury is then rubbed into the plates with the aid of ammonium chloride or potassium cyanide, and then they are given a coat of freshly prepared silver amalgam. Sometimes they are first silver-plated in order to give a better surface for the application of the mercury.

397. Operation. The plates, thus carefully prepared, are then placed in position in front of the stamp mill. When in operation they are usually dressed about every four hours in order to keep the surface in proper condition. The intervals of dressing will be regulated by the richness of the ore. When the amalgam has become so hard that, in the judgment of the operator, it is not catching all the gold, the ore and water are shut off and the stamp is shut down. With a small scraper or hoe the readily removable amalgam is scraped off into a container. From a small

bottle, with a perforated stopper, fresh mercury is sprinkled on the surface of the table and worked into the pores, and the battery is ready to start once again. The amalgam must be of the proper consistency. It should not be so wet or so soft that it will be washed away by the pulp current, nor yet so dry that it will not readily absorb gold. The amount of water added with the ore must be such that the pulp flows in ripples, slowly and steadily, down over the plates. No part of the plate should be allowed to become dry.

The loss of mercury will vary from $\frac{1}{4}$ to 1 ounce per ton of ore treated. Most of this loss is due to "flouring" or "sickening." Mercury is said to be floured when it is divided into such fine particles that these will not unite with gold or stick to the surface of the amalgamating table. It is said to be sickened when it is in a similar fine state of division and in addition is covered with a film of oil or grease which prevents its coming in contact with the gold. These difficulties may be caused by impure mercury, contact with grease or oil, or excessive stamping.

If the plates become tarnished or covered with a coat of basic carbonate, as often happens in amalgamating copper ores, this coat can be removed by means of ammonium chloride or potassium cyanide. Spots thus cleaned should be immediately re-dressed with fresh mercury.

The pulp, after it has passed over the amalgamating plates, may be sent to waste, but usually the recovery by amalgamation is so low that it must be re-treated by cyanidation or chlorination to recover the remainder of the gold. In the early days of gold mining the operators relied entirely on amalgamation.

The interval between clean-ups will depend upon the richness of the ore. Ordinarily it takes place about twice a month. In case inside amalgamation is practiced, the mortar and dies are carefully scraped and cleaned of amalgam, and this is added to that recovered from the plate. To this amalgam, which usually contains sand, pyrite, fragments of iron, etc., is added fresh mercury and water, and the whole is agitated in a barrel or stirred in an amalgamation pan. The impurities rise to the surface and may be skimmed off. The amalgam is strained through canvas to free it of excess mercury, and after this operation it will be hard and dry and will contain approximately 40 per cent of Au.

The clean amalgam is then charged into a cylindrical iron retort and by the application of heat the mercury is distilled off, leaving the gold in the retort. This residue is melted with suitable fluxes and cast into bars. The distilled mercury, together with that taken off in the amalgam press, may be used again on the plates.

398. Recovery of gold. The recovery of gold by amalgamation is low, ranging from 50 to (under exceptional circumstances) 70 per cent of the total gold. The chief losses of gold are due to the following causes:

1. Float gold, which is so finely divided that it is swept along with the pulp into the tailings.
2. Rusty gold, which is covered with iron oxide or gangue so that the mercury does not have an opportunity to act on it.
3. Floured mercury, which carries along with it some dissolved gold.
4. Mechanical loss of amalgam.
5. Particles of ore containing gold.
6. Losses in sulphides and tellurides which are not amenable to amalgamation.
7. Loss in the tailings.

This process is fast losing its popularity, owing to its comparative inefficiency. It is commonly used as a secondary process whenever a considerable portion of the gold may be thus easily won. It is easier and cheaper to recover, let us say, 30 per cent of the gold in this way than it is to go through the long and expensive process of cyaniding or chlorinating the ore.

CHLORINATION

399. General. This process depends upon the fact that chlorine has a strong affinity for gold and combines with it to form soluble gold chloride. The rock minerals and most metallic compounds which occur with the gold, such as hematite, galena, arsenopyrite, etc., are unaffected. The solution containing the gold may then be separated from the valueless gangue by decantation or filtration, and the gold precipitated and refined. The two methods by which this process is carried out are the vat, or Plattner, process and the barrel process. They are chiefly of historic interest, having been largely displaced by cyaniding.

400. The barrel process. This process is carried out in large steel barrels, 6 feet in diameter and 16 feet long, holding about 12 tons of ore. These barrels are lined with sheet lead $\frac{1}{2}$ inch thick and designed to withstand a pressure of 100 pounds per square inch. They are supported by and revolved on two trunnion bearings. The barrel is fitted with a false bottom or internal filter so that the ore may be chlorinated, leached, and washed in the apparatus itself. The filter consists of a finely perforated sheet of 6-pound lead laid on lead plates $\frac{1}{2}$ inch thick which are perforated with $\frac{3}{8}$-inch holes. The whole is held together with two gratings of hard wood. There are two openings in the top of the barrel, for charging the ore and reagents, and valves in the bottom, below the filter, for draining off the solution and washings.

The chlorine is generated from bleaching powder according to the following reaction:

$$CaOCl_2 + H_2SO_4 = Cl_2 + CaSO_4 + H_2O.$$

The barrel is first charged with enough water to give a pulp of the proper consistency for efficient mixing. Sulphuric acid is poured into the container in such a manner that it does not mix with the water but forms a layer on the bottom of the barrel. Ore, ground to about 8 mesh, is then charged in and the proper amount of bleaching powder placed on top of the ore. The barrel is sealed and revolved at a rate of from three to six revolutions per minute for from three to six hours. When chlorination is complete (this can be determined only by experiment), the barrel is stopped, with the filter bottom down, and the ore is allowed to settle out. The discharge pipe is opened and the clear solution, which has collected below the filter, is allowed to run out into storage vats for clarification and precipitation. Water is then pumped in, and the barrel is again revolved in order to wash out the soluble gold chloride. This procedure is repeated until the washings no longer give a test for gold.

The solution containing the gold chloride is clarified and then treated with sulphur dioxide in order to neutralize the excess chlorine:

$$Cl_2 + SO_2 + 2\,H_2O = H_2SO_4 + 2\,HCl.$$

Unless this is done there would be an excessive consumption of H_2S, owing to the decomposition by the chlorine.

Precipitation of the dissolved gold is effected by hydrogen sulphide according to the following reaction:

$$2\ AuCl_3 + 3\ H_2S = Au_2S_3 + 6\ HCl.$$

Ferrous sulphide was used at first, but the precipitate produced by it required a long time for complete settlement. Complete precipitation can be effected with H_2S. After precipitation the solution is passed through a filter press, and the precipitate is washed and dried. The cakes of gold sulphide are given an oxidizing roast in order to drive off the sulphur. This calcine is mixed with the proper fluxes — usually sodium carbonate, niter, and borax — and smelted to gold bullion and slag. The extraction by this process may run as high as 95 per cent of the gold, but will average considerably less than this figure. The gold bullion will be from 900 to 950 fine.

401. The vat process. This is interesting solely from a historical standpoint. It is now obsolete in this country, having been replaced by either the barrel process or the cyanide process. The ore is crushed to about 10 mesh and then roasted with common salt. The object of roasting is to expel S, As, Sb, and other volatile constituents and to convert the base-metal compounds into chlorides and thus avoid a waste of chlorine later. There is a loss of gold, owing to the volatilization of the chloride; hence salt should be used only if necessary. The roast should then be carried out at as low a temperature as possible. The calcine is next charged into a large vat with a filter bottom and a tightly fitting cover, and freshly generated chlorine gas is passed up through the filter bottom. Filtration and precipitation are similar to the barrel process.

THE CYANIDE PROCESS

402. General. This process consists in treating the finely ground ore with a dilute solution of potassium or sodium cyanide. The solution generally contains less than 0.5 per cent of the salt, but such weak solutions readily dissolve the gold and silver, leaving most of the base-metal compounds unaffected. There are some of the latter (cyanicides) that are acted on by the cyanide and cause an excessive consumption of the reagent. The solution containing the gold can then be separated from the ore and the gold precipitated and refined. For

the purpose of this textbook the cyanide process will be divided into the following basic steps: (1) preparation of the ore, (2) sand leaching, (3) slime treatment, (4) filtration, (5) precipitation, (6) refining.

Preparation of the Ore

403. General. The nature of this process will depend upon the character of the ore and upon the state of division of the gold. In some ores the gold occurs in fairly coarse particles, or the ore is porous enough to permit the cyanide solution readily to penetrate the particles and dissolve the gold. Such ores may give an excellent extraction when crushed to pass a 30-mesh screen. With other ores the gold is finely divided or the gangue dense and so impermeable to the solution that in order to free the gold the ore must be reduced to a very fine state of division, let us say so that 85 per cent of it will pass a 200-mesh screen. Such an ore is said to have been slimed, and the scheme of treatment is called the slime process in contradistinction to the sand-leaching process.

The following methods for preparing the ore for treatment are in common use today:

1. Crushing the ore in water with stamp batteries to pass a 20-to-30-mesh screen. The ore may then be amalgamated and separated into a sand and a slime, and each of these products may be treated separately.

2. Crushing the ore in water with stamp batteries to pass a $\frac{1}{2}$-inch to 10-mesh screen, classifying the pulp, and grinding the oversize to the required state of division in ball or tube mills. The ground product is separated into a sand and slime, and each is treated separately.

3. Crushing the ore as in 2 and then grinding the whole to pass a 100-to-200-mesh screen; that is, to a slime.

4. Crushing the ore by either 1, 2, or 3, but in cyanide solution instead of water.

For the crushing of gold ores the machinery already described in Chapter VI, "Preparation of Ores," is in common use in the United States. In recent years there has been a tendency on the part of certain operators to give up the stamp mill in favor of coarse crushing in gyratory breakers or Symons crushers, followed by fine grinding in ball mills and tube mills. They claim

that such a combination gives a lower operating cost, greater freedom from repairs, and more flexibility. This may be true for certain ores, but it is a significant fact that some of our latest gold mills still use the California stamp mill.

404. Concentration. It is common practice to carry on gravity concentration before cyaniding. A considerable portion of the sulphide material can thus be removed as a concentrate and shipped to a smelter for reduction in a blast furnace. The tailings from gravity concentration can then be cyanided in the usual manner. The result will be a greater recovery of the gold and a much lower cyanide consumption than there would be if the entire ore were cyanided. Sometimes there is not sufficient margin of profit to permit concentration, for it adds to the initial cost of the plant as well as to the cost of the whole operation.

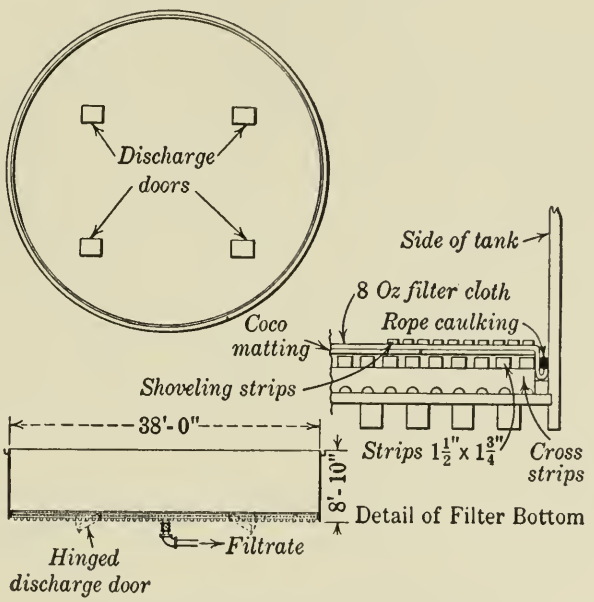


FIG. 124. A sand-leaching tank

SAND LEACHING

405. General. Many clean quartzose ores can be readily treated by leaching. In this process the ore pulp, after crushing and grinding, is separated into a sand and a slime. The sand is treated in leaching tanks by percolation, while the slime is agitated in some form of mechanical agitator and the pregnant solution separated from the worthless tailing by filtration.

The leaching vats for sand are constructed of wood or steel and provided with a filter bottom. Wood is to be preferred in the construction of these as well as any other containers around the cyanide plant; for steel tanks, unless considerable care is taken with painting and preservation, rust and corrode very rapidly. A common type of sand-leaching tank is shown in Fig. 124. A ring of wood about 3 inches high and 3 inches wide is fixed

to the bottom of the tank, about $1\frac{1}{2}$ inches from the sides. Within this space is constructed a latticework of hard-wood slats, crisscrossed so as to leave ample space for the solution to find its way to the discharge valve. Upon this latticework is laid coco matting, and on top of this a filter cloth of heavy canvas. This filter medium extends to the wall of the tank and is held in place by a rope driven down into the outside annular space. Very often it is protected by "shoveling strips." In small tanks there is one central discharge door; in larger tanks there may be from four to six. These tanks vary in size from 16 to 50 feet in diameter and from 4 to 9 feet in depth.

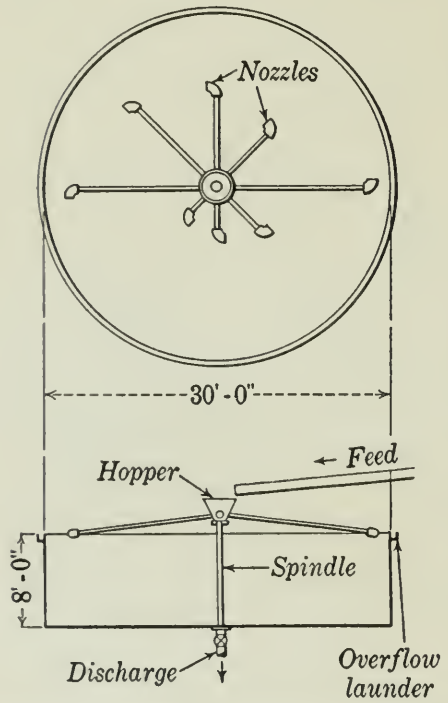


FIG. 125. The Butters distributor

At some plants the sand to be cyanided is first run into a collector tank. This tank is filled with clear water and the sands from the classifier are run into it until it is full of settled sand. The overflow is sent on to the slime department. Such a collecting tank with a mechanical distributor is shown in Fig. 125. When the tank is nearly full of clean sand the flow of pulp from the mill is stopped and the water is siphoned off. Cyaniding may then be carried on in this tank or it may be used for storage, the contents being transferred to leaching tanks as required.

Along with the sand are added lead acetate ($\frac{1}{2}$ pound per ton), slaked lime (4 pounds per ton), and sufficient cyanide to bring the resulting solution up to about 0.25 per cent strength. After it has leached for some time, the drain cocks are partly opened and this first leaching solution is allowed to drain off slowly. It is followed by weak solutions of cyanide and finally by wash water. Each change of solution is allowed to sink below the level of the sand in the tank before the next is added. The total time of treatment will range from twelve to eighteen days according to the richness of the ore and the ease of leaching.

Some ores contain so much kaolin, gelatinous silica, or aluminum compounds that they are not amenable to sand leaching, owing to the fact that the rate of percolation is so slow. All the leachings are collected and kept in storage tanks. The strong solutions are so rich in Au that they may be sent directly to the precipitation plant; solutions low in Au but high in KCN are used as the first leaching solution of the next batch, while the wash water is used as a base for making up fresh cyanide solution. The solid KCN may be dissolved by being suspended in a basket in the leaching tank or it may be made up in a small tank as strong solution and added as conditions require.

The sand, after the leaching is completed, may be removed from the tank by shoveling or sluicing or by a mechanical excavator. The Blaisdell excavator is probably the best, although it is a large and expensive machine to install and is not suited to small plants. It consists of a massive traveling bridge carrying the excavating machine. This consists of a central vertical shaft carrying horizontal arms to which are attached plows or rakes similar to the Dorr-thickener mechanism. This is lowered into the tank until the rakes touch the sands. As the arms revolve the sand is worked toward the center and drops through the discharge door into a launder or upon a belt conveyor. By means of the traveling bridge the whole mechanism can be raised and transferred to another tank. The capacity of such a machine is from 50 to 180 tons per hour.

Sand leaching has been given up in the United States, for it has been found that most of our ores are more cheaply and efficiently treated by the agitation process. On the Rand, in South Africa, many large plants still use the leaching method, but they operate under the special conditions of a clean quartzose ore, which produces, with suitable grinding, very little slime. Furthermore, these plants were designed for such treatment, and the operators hesitate to scrap the machinery in favor of the agitation process. Even there, however, there is a distinct trend toward the all-slime method.

Slime Treatment

406. General. Unfortunately the term *slime* has never been exactly defined. According to one authority it may be defined as that portion of the ore which, owing to its very finely divided

condition or to the presence of colloidal substances, settles very slowly in water and cannot be leached by the ordinary process of sand leaching. More generally, slime is regarded as that portion of the ore which has been crushed so that it will pass a 200-mesh screen, — that is, into particles less than 0.003 inch in diameter. Such a pulp, if allowed to settle in a filter-bottom tank, will soon blind the interstices of the fabric so that very little solution will pass. In order to bring the particles of ore in contact with fresh solution the pulp must be agitated, either mechanically or by air. Separation of the pregnant solution from the worthless gangue is effected by means of some form of pressure or vacuum filter. Three methods are used for dissolving the gold and recovering the valuable solution: (1) simple decantation, (2) countercurrent decantation, (3) agitation. The choice of the method to be employed will be governed entirely by the character of the ore and its precious-metal content.

407. Decantation. This process is carried out in a series of collection vats. These are tanks, about 50 feet in diameter, with conical bottoms and fitted with annular launders to collect and carry off the clear overflow during the filling period. The stream of pulp is fed into the center of the tank at such a rate that when the tank is filled with pulp the slime will have settled to some extent and there will be a clear overflow. It is common practice to add lime to the pulp before it enters the collector. An excess of lime is always required for the cyanide process, and the presence of this during the decantation period promotes settling. The amount added will depend upon the presence of acid-forming constituents in the ore, about 6 pounds of lime per ton of ore being an average figure.

When the collector is full the clear solution is siphoned off by means of a decanter. This is a 3-inch pipe, hinged where it passes through the side of the tank near the bottom. By means of this hinged joint it is possible to keep the inlet of the pipe just below the surface of the clear water in the tank, and thus avoid siphoning off any slime. When clear water has been removed, the slime is sluiced out with cyanide solution and transferred either by gravity or by a pump to the first-treatment vat.

In the first-treatment vat the slime is kept in suspension and agitated for from four to six hours. This may be done by keeping the material in circulation by a centrifugal pump or by some

form of mechanical agitator suspended in the tank. When agitation is complete, the slime is allowed to settle again and the clear solution is siphoned off as before. This contains the major portion of the gold and silver, and after passing through a clarifying press or tank it is sent to the zinc boxes for the precipitation of the gold. The strength of the cyanide solution will vary from 0.005 to 0.3 per cent KCN according to the character of the ore. After this solution has been removed the slime is sluiced out with barren cyanide solution into a second-treatment vat, where the process is repeated. This solution, however, contains but little Au or Ag and is not sent to the precipitation plant. It is used to sluice the pulp from the collector vat to the first-treatment vat. Usually there is a third-treatment vat, in which the pulp is washed with water before being discharged into the slime pond.

It is obvious that the decantation process requires a large number of tanks and considerable valuable plant space, that it ties up a large tonnage of ore, and that it allows an excessive amount of soluble gold and cyanide to escape with the tailings. It has the advantage of dispensing with an expensive filtration plant, but this is not enough to compensate for the disadvantages mentioned above. As a result very few decantation plants are in operation today. A modified form, the counter-current decantation system, is in common use today and is bidding strongly for favor against the filtration processes.

408. Thickening. The slime pulp as it comes from the sand classifier is too dilute for efficient handling by any of the agitation processes. Such pulp will range from five to ten parts of solution to one part of dry slime. It should be thickened to about 50 per cent moisture before treatment. There are several reasons for this. If the grinding is carried out in water, the dilute pulp could be brought up to strength by the addition of sufficient cyanide, but the resulting solution would be too low in precious metals for efficient precipitation. It would also mean the handling of a much larger bulk of material, with a consequent increase in agitation and filtering costs. Such thin pulps give considerable trouble in agitation, owing to the fact that the heavy or coarse particles settle out readily and tend to clog or choke these devices. Again, for efficient filtration, the moisture should first be reduced to as low a point as possible.

The Dorr continuous thickener is almost universally used for thickening pulps in the cyanide process. This piece of apparatus has already been described in Chapter VI, "Preparation of Ores." With careful attention the moisture in the discharge of a thickener may be reduced to as low as 33 per cent.

In practice it has been found that with this type of thickener, treating a pulp with from 75 to 90 per cent of moisture, the area per ton of solids thickened per twenty-four hours averages about 4 square feet for a clean siliceous ore, but may rise as high as 15 square feet for an ore containing kaolin or colloidal material.

409. Agitation. The agitation of a slime pulp is carried out for the purpose of bringing it in more intimate contact with the cyanide solution and furnishing the air necessary for the solution of the gold and silver. This agitation is usually effected in conical or flat-bottomed tanks by means of injected air or some mechanically driven arm or propeller blade. A great many devices have been suggested and tried, but of these only the Pachuca and the Trent and Dorr agitators will be described.

410. The batch versus the continuous system. In many cyanide plants a tank is filled with properly ground pulp and this is treated as a batch, or unit; that is, it will be agitated and filter-pressed as a unit without the addition of any fresh pulp. In other plants (and an increasing proportion, for that matter) the continuous system is in use. The pulp from the mill enters the first of a series of Pachuca tanks or Dorr agitators and flows continuously through the system. The advantages claimed for the continuous system are (1) an increase in the time of agitation for any given unit of capacity and (2) less labor and attention. There are only two serious disadvantages: (1) There is danger of short-circuiting; that is, some of the pulp may get through with too short a time of contact with the solution. (2) When Pachuca tanks are kept full of pulp over long periods of time, a deposit of lime and hard slime builds up on the inside of the tanks, and this reduces the capacity of the tanks and the time of treatment.

411. Pachuca tanks. This type of agitator operates on the principle of the common air lift. In Fig. 126 such a tank is shown in vertical cross section. It consists of a steel cylinder

33 feet high and 10 feet in diameter, with a cone-shaped bottom to facilitate the removal of the residue. At the apex of the cone is a large gate valve through which the contents of the tank may be discharged at the end of the agitation period. In the center of the tank is the air lift, or standpipe. This is a pipe 10 inches in diameter, open at both ends, and extending from about 2 feet above the apex of the cone to just above the level of the pulp in the tank. This standpipe is braced firmly against the sides of the main tank. At the center of the lower opening of the standpipe is a small pipe which admits a jet of compressed air, controlled by a valve located at the top of the tank. The air lift thus formed raises the pulp in the standpipe and discharges it at the top of the tank, thus effecting a very efficient agitation and circulation. While the tank is being filled the air lift will of course not operate, and there is a tendency for the pulp to pack around the mouth of the standpipe and choke it. One way to overcome this difficulty is to bubble air through the mass of pulp in the bottom of the tank and keep it in suspension. Another is by means of a spider with four arms, which may be lowered over the standpipe to the level of the settled pulp in the tank. Then by slowly rotating this spider and at the same time forcing air through the arms it may be made to bore its way down into the settled mass of slime and free the entrance to the standpipe.

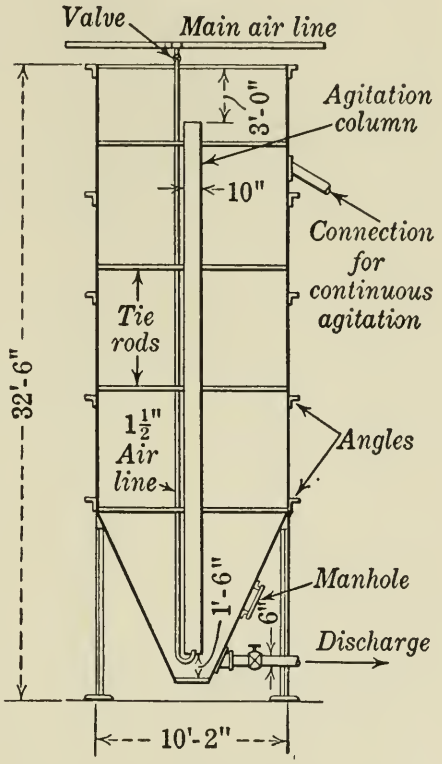


FIG. 126. Pachuca tank

The Pachuca tank is a simple and efficient device for agitating pulp, but the large amount of head room or mill head necessary has always been a drawback. Another disadvantage is the large amount of air necessary to agitate the pulp over what is necessary for the chemical reaction of dissolving the precious

metals. In spite of this the power requirements are small. An installation of ten tanks, each 10×39 feet, treating a slime, required 88 cubic feet of free air per minute, at a pressure of 25 pounds per square inch. Each tank held a charge of 35 tons (dry weight).

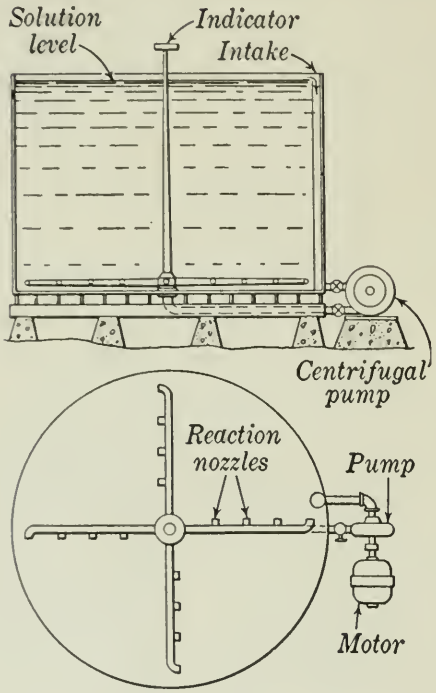


FIG. 127. The Trent agitator

412. Trent agitator. The Trent agitator is shown in Fig. 127. It consists of a flat-bottomed tank in the center of which is a vertical shaft supporting four arms about 18 inches above the bottom of the tank. The arms are hollow and carry a row of nozzles inclined at a slight angle to the bottom of the tank. The circulation is effected by means of a centrifugal pump mounted outside the tank. This pump draws pulp from the surface of the liquid in the tank and forces it into the arms. The force of the discharge through the nozzles causes the arms to revolve. The aëration of the charge is accomplished by drawing air in with the pulp at the suction inlet or injecting high-pressure air into the pulp as it goes to the arms. The power consumption is probably a little higher than that of the Pachuca tank. At one plant the agitation of 100 tons of dry slime per day requires only 12 horse power.

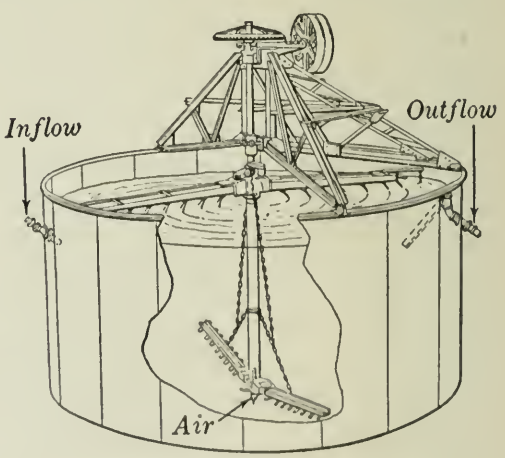


FIG. 128. The Dorr agitator

413. Dorr agitator. Another agitator enjoying considerable popularity is the Dorr. It is a development of the Dorr thickener, the difference being that the rakes revolve at from one to three revolutions per minute instead of once every five to ten minutes. This piece of apparatus is shown in Fig. 128.

The central revolving shaft is hollow and, besides the standard Dorr arms at the bottom, carries at the top a pair of launders. The bottoms of these launders are perforated at regular intervals so that the pulp may be distributed evenly over the surface of the tank. The central shaft is hollow, somewhat larger than in the standard mechanism, and serves as an air lift to transfer the pulp from the bottom to the top of the tank.

In operation the pulp flows in continuously at some point in the periphery of the tank and is led by a downcast pipe almost to the bottom. There is very little agitation by the slowly revolving arms, so that the pulp settles to the bottom, is gathered by the rakes to the center of the tank, and is elevated by the air

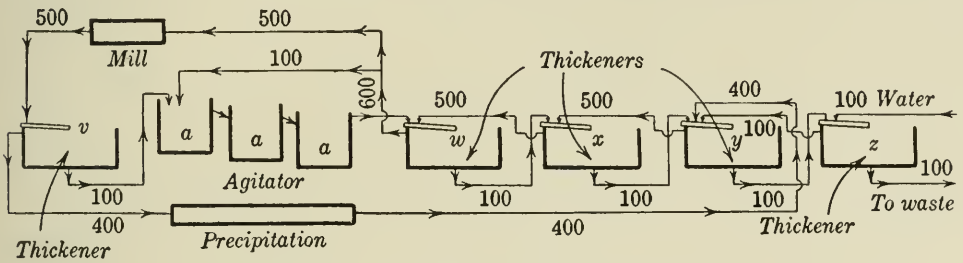


FIG. 129. Countercurrent decantation

All figures refer to solution tonnages

lift to the revolving distributor above the surface. It makes this circuit a number of times before the entrance of fresh material displaces it through the outlet pipe. It has the advantage of "selective agitation," in that coarse particles, which require a longer time of treatment, sink more rapidly to the bottom and thus make the circuit a greater number of times. About the only disadvantage lies in the fact that it is not suitable for the batch system of treatment; it is essentially a continuous machine.

414. Countercurrent decantation. The Dorr agitator is admirably adapted to the system known as countercurrent decantation. This endeavors to dispense with the expensive filtering operation and is fast gaining favor with metallurgists. A series, usually four, of Dorr tanks is required for the process. Each thickener is placed at a slightly lower elevation than the next preceding, so that the clear overflow may flow back by gravity. As indicated in Fig. 129, there are two separate currents, the clear solution working its way toward the head tank and dissolving precious metals as it goes, and the pulp traveling

toward the tail tank, where it is discharged. Very often, particularly with ores requiring a long time of treatment, the Dorr system is preceded by some continuous-agitation system. As indicated by the sketch, the ground pulp from the mill goes to thickener v. The clear overflow of v goes to the precipitation plant; the spigot of v is raised by a diaphragm pump to the agitators a and forms part of the feed of w. The clear overflow of w goes to the mill; the spigot of w is raised by a diaphragm pump and forms part of the feed of x. The clear overflow of x is used to dilute the feed of w; while the spigot of x is raised by a diaphragm pump and forms part of the feed of y. The clear overflow of y is used to dilute the feed of x; while the spigot of y is raised by a diaphragm pump and forms part of the feed of z. The clear overflow of z is used to dilute the feed of y; while the spigot of z goes to waste or may, if necessary, be treated in filter presses. Water in sufficient amount to make up for losses in the system is added to z along with the spigot of y. Barren solution from the precipitation plant is added to the feed of y.

The following calculation, from a pamphlet issued by the Dorr Company, is given to show the change in the composition of each tank in the series. In the calculation it is assumed that 75 per cent of the metal goes into solution during the milling process.

Calculations for Dissolved-Value Loss

Conditions assumed:

1. 100 tons of ore per day crushed in cyanide solution.
2. Discharge from all thickeners with 50 per cent of moisture.
3. \$10 value dissolved per ton of ore.
4. 75 per cent in mill and 25 per cent in agitators.
5. 400 tons of solution from thickener v precipitated to \$0.02.
6. Agitation with a dilution of two of solution to one of solids.
7. Let V, W, X, and Z represent value in dollars per ton of solution discharged from their respective thickeners.

Equating out of and into each thickener:

1. $100\ V + 400\ V = 500\ W + (0.75 \times \$10 \times 100)$.
2. $100\ W + 600\ W = 500\ X + 100\ W + (0.25 \times \$10 \times 100) + 100\ V$.
3. $100\ X + 500\ X = 100\ W + 500\ Y$.
4. $100\ Y + 500\ Y = 100\ Z + 100\ X + (400 \times \$0.02)$.
5. $100\ Z + 100\ Z = 100\ Y + 100$ tons of water @ \$0.00.

Simplifying:	Solving:
1. $V = W + 1.50$.	$V = \$2.51332$.
2. $W = X + 0.80$.	$W = 1.01332$.
3. $X = Y + 0.16$.	$X = 0.21332$.
4. $Y = 0.2\ Z + 0.048$.	$Y = 0.05332$.
5. $2\ Z = Y$.	$Z = 0.02666$.

From the foregoing the following results are deduced:

Assay value of the pregnant solution = \$2.51332.
Assay value of the discharged solution = 0.02666.
Loss of dissolved value per ton of ore = 0.02666.
Dissolved value saved, 99.7 per cent.

Calculation of Mechanical Loss of Cyanide

Conditions assumed:

1. Neglect the cyanide consumption throughout the system.
2. Strength of cyanide per ton of solution, 1.0 pound.
3. Let V, W, X, Y, and Z represent the strength in pounds of cyanide in solution discharged from their respective thickeners.

Equating out of and into each thickener:

1. $V = 1.0$.
2. $100\ W + 600\ W = 100\ W + 100\ V + 500\ X$.
3. $100\ X + 500\ X = 100\ W + 500\ Y$.
4. $100\ Y + 500\ Y = 100\ Z + 400\ V + 100\ X$.
5. $100\ Z + 100\ Z = 100\ Y + 100$ tons of water.

Simplifying:	Solving:
1. $V = 1.0$.	$V = 1.0$.
2. $6\ W = 5\ X + 1$.	$W = 0.9109$.
3. $6\ X = W + 5\ Y$.	$X = 0.8932$.
4. $6\ Y = Z + X + 4$.	$Y = 0.8898$.
5. $2\ Z = Y$.	$Z = 0.4449$.

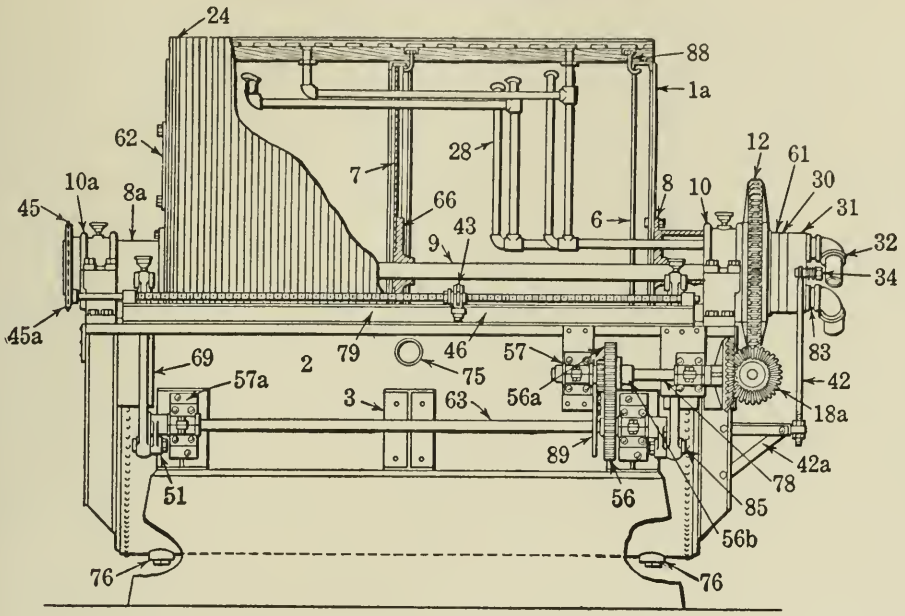
Mechanical loss of cyanide per ton of ore = 0.4449 pound.

The countercurrent system is best adapted to low-grade quartzose ores that are easily leached and settled. The greatest objection is the mechanical loss of cyanide, especially when treating silver ores requiring a concentration of cyanide higher than 0.1 per cent. For this reason it is often supplemented by a dewatering filter. The cost of operation is low and the relative simplicity of the plant, freedom from repairs, and low cost of labor make it a very attractive system.

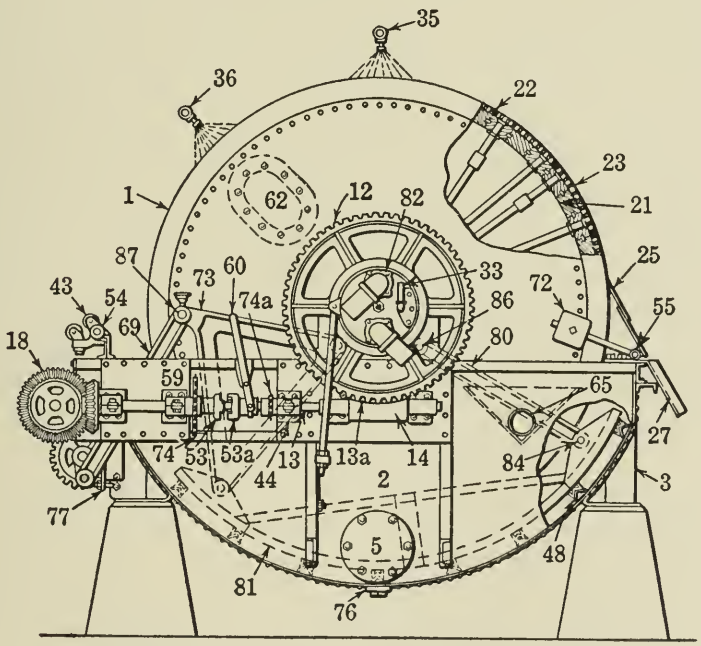
Filtration

415. General. By filtering is meant the separation of the valuable cyanide solution from the worthless residue. It is one of the most vital steps in the whole cyanide process, for not only must the separation be as complete as possible, but the cost of the operation should not constitute more than 5 per cent of the total cost of treatment. It would be quite simple to remove all of the soluble values as well as the cyanide from the pulp, but it would be difficult to do this and yet make a profit on a low-grade ore. The character of the pulp to be filtered has much to do with the type of filter used and the degree of success of the operation. If the ore is too coarse, it will increase unduly the power consumption in the agitators and thickeners, will tend to choke the pipes and pumps about the plant, and will cause uneven washing through channeling and classification. A pulp with a high percentage of fine material is also very hard to handle. It is seldom possible to thicken such a pulp to less than 60 per cent moisture, and a product with this amount of moisture takes a long time to filter and wash, and considerably reduces the capacity of the machine. With high percentages of fine material it is seldom possible to build up cakes thicker than $\frac{1}{2}$ inch. Under such conditions the filter operates well during the first few minutes of the cycle; then the filter medium chokes, and even with considerable pressure it is almost impossible to force more solution through. Washing, of course, is equally difficult. For ideal filtering the pulp should be ground so that not more than 25 per cent will remain upon a 200-mesh screen. On the other hand, it should be free from amorphous or colloidal material, so that it will settle from 85 per cent water to 50 per cent with a settling area of from 6 to 10 square feet per ton of dry solids per day. There are a great many mechanical filters on the market today, but only those in most common use in metallurgical plants will be described in this text, — the Oliver, Kelly, Merrill, American, and Dorrco. The filters can be divided into the following classes: (1) vacuum filters, (2) pressure filters, (3) continuous decantation.

416. Oliver filter. This filter is of the continuous vacuum type. A modern filter is shown in Fig. 130. It consists of a



Filter with Oscillating Agitator and Enclosed Heads
Designed for Electric Motor Drive



Filter with Oscillating Agitator and Enclosed Heads
Designed for Electric Motor Drive

FIG. 130. Oliver filter press

slowly revolving drum, or cylinder (1), the axis of which is horizontal. The lower portion of this drum is submerged in a tank (2) containing the pulp to be filtered. At each end of the horizontal shaft are trunnions which serve to support the drum. The outside of this drum is hollow, consisting of an outside filter medium (23) and an inner supporting surface of wood, steel plate, brass, or acid-resisting alloy which is impervious to liquids and air. The space between the inner and the outer surface is divided into shallow compartments by division strips which are parallel to the axis of the drum. Between the strips and the outer filter medium is placed a supporting surface of screen or grating. The filter medium is of cotton, wool, or metal, depending upon the character of the pulp being filtered and the kind of product desired. In all filters this filter medium is held in place on the drum by an evenly spaced wire winding (24) which encircles the drum spirally. This also serves to protect the cloth from the wear of the scraper (25), which helps to remove the cake.

Each compartment of the drum shell is connected by a system of piping (28) with the automatic valve that controls the application of vacuum to the filter and the admission of compressed air or steam for "blowing" the discharged cake. This automatic valve (31) controls the entire cycle of cake formation, washing, drying, and discharging and is composed of two main parts, the valve seat and the valve chamber. The former is bolted to the drum trunnion; the latter is held in a fixed position. By a simple adjustment each compartment may be subjected to different periods of cake formation, drying, and washing.

Rotation of the drum is effected by a worm gear (12) driven by a motor. The speed of the drum will vary from one minute to ten minutes per revolution. In the older type of Oliver filter the material in the tank was kept in suspension by means of a horizontal revolving shaft with short arms. This shaft was located in the bottom of the tank. This arrangement, particularly with coarse, heavy pulps, gave a great deal of trouble, because the material settled out around the arms, threw off the drive belt, or stripped the gears. The new method of agitation is with an oscillating agitator (81). This consists of horizontal rakes mounted on arcs which slowly oscillate with the drum center as an axis, so that the travel of one rake

overlaps that of the next. The object of this is to maintain a thorough mixture of the pulp, prevent settling, and insure a homogeneous filter cake. As the drum rotates, the filtering surface is passed through every part of the agitated mass. Immediately each compartment under vacuum is immersed; a cake begins to build up and continues to form until the drum emerges from the pulp. The liquid passes through the filter medium and the vacuum pipes to the automatic valve, while the solid particles adhere to the drum surface in a uniform cake. As solids are removed from the tank the level of the pulp may be kept constant by an automatic float or it may be replenished from time to time by the operator.

TABLE XLII. CAPACITIES OF OLIVER FILTERS (IN POUNDS PER SQUARE FOOT PER TWENTY-FOUR HOURS)

MATERIAL	MINIMUM	AVERAGE	MAXIMUM
Ore slime-cyanide process	200	400	1500
Flotation concentrate	200	600	2000
Magnetic iron concentrates	2000	3000	4000
Cold saccharate of lime (weight of molasses)	200	220	250
Hot saccharate of lime (weight of molasses)	1000	1200	1500
Lime mud (first carbonation, weight of beets)	2000	2500	3000
Lime mud in causticizing plants	500	750	1000
Bicarbonate of soda, ammonia process	2000	2500	3000
Calcium sulphate precipitates	400	600	800
Prepared clay for oil refining	400	500	600
Lubricating oil, clarified	200	350	600
Residuum from cracking process	600	800	1000
Paper pulp, thickening and brown stock washing	500	800	1000
Starch	800	1000	1200
Fine coal	1000	1500	2000
Activated sludge, sewage disposal	10	15	20

For washing the cake either sprays or drip pipes (35, 36) located just above the upper surface of the drum may be used. Washing is very efficient, for the cake is seldom more than $\frac{1}{2}$ inch in thickness. As soon as a compartment passes out of the washing zone the vacuum dries the cake before it is discharged. Revolving beaters are sometimes used to pat the cake lightly and thus force out a little more moisture. When a given section approaches the scraper (25), the vacuum is automatically cut off, compressed air is admitted, and the cake is loosened from the filter medium and discharged over the scraper, thus

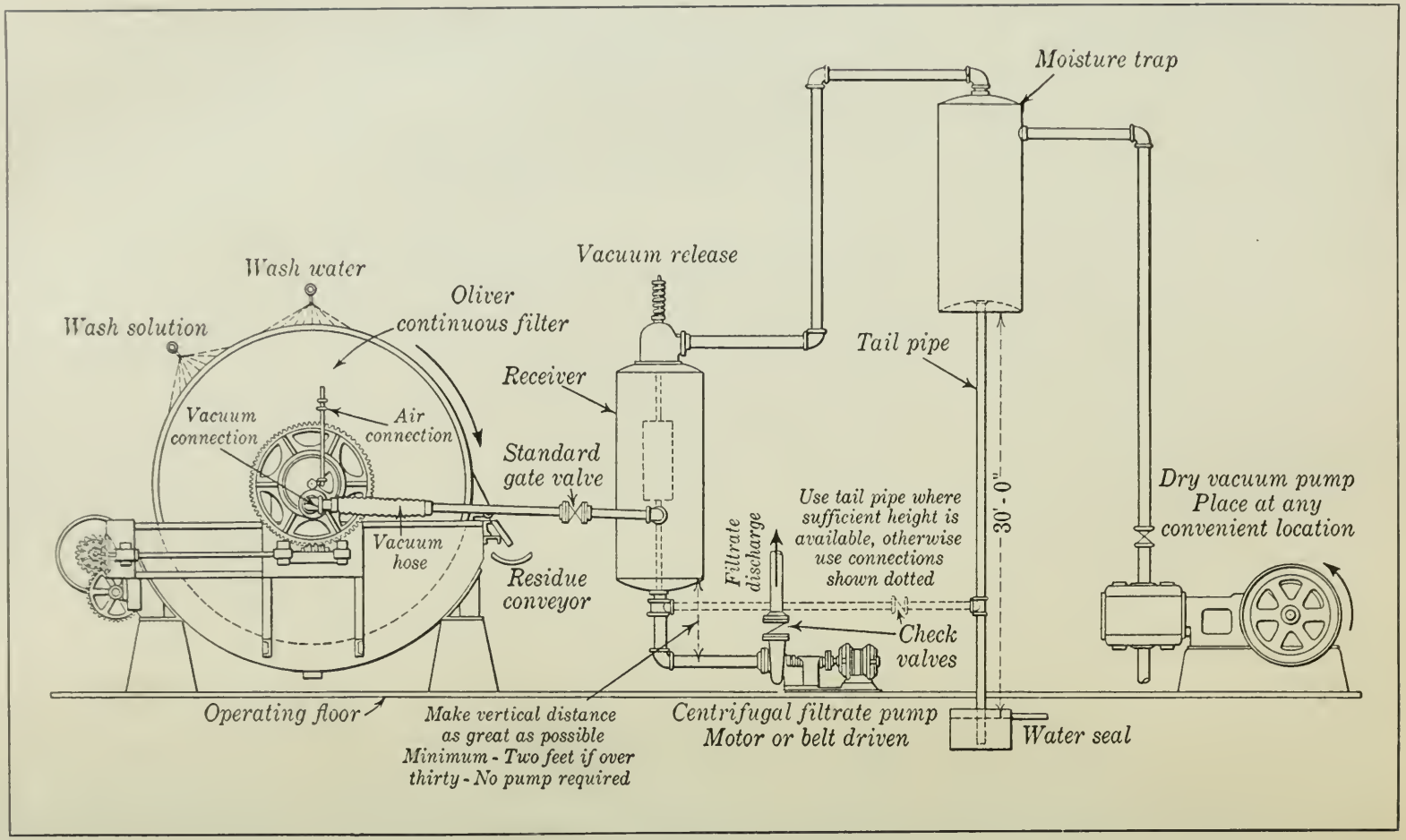


FIG. 131. Oliver-filter-press installation

leaving a clean filtering surface which passes downward into the pulp for a new cycle. Table XLII, on page 317, gives, in pounds, the amount of material that can be handled per twenty-four hours on 1 square foot of filter surface.

For maintaining the vacuum either the wet or the dry system may be used. A dry vacuum pump differs from a wet one in that no clearance is allowed for solution, as nothing but air

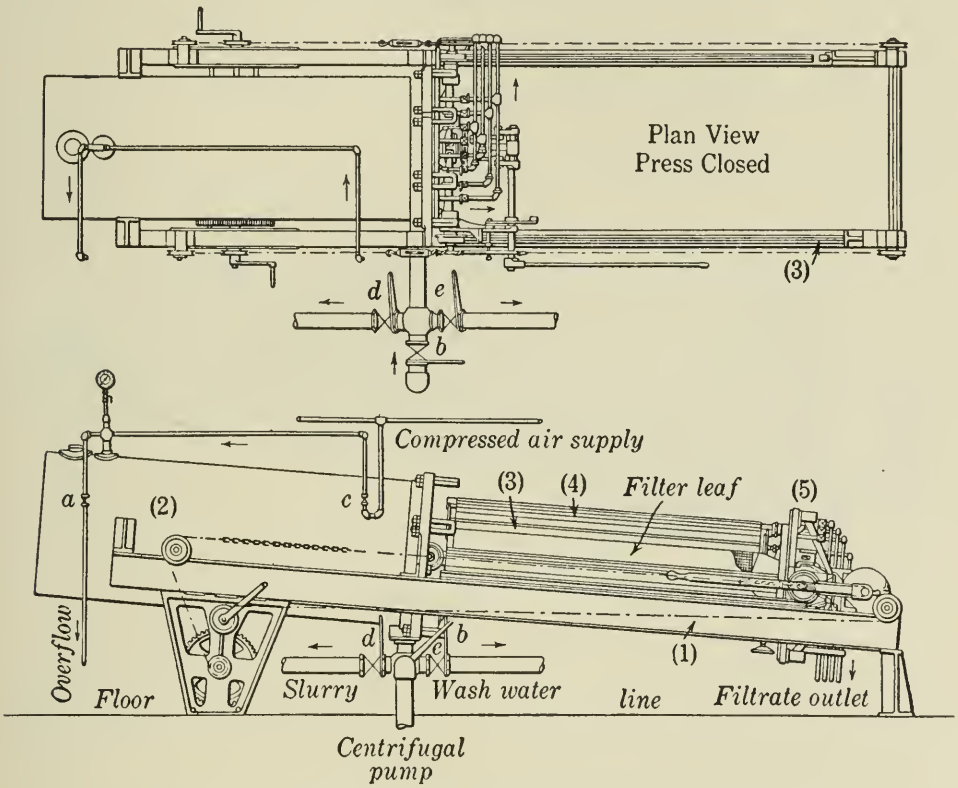


FIG. 132. Kelly filter press (side view, press open)

passes through it. The dry system is not only preferable from a standpoint of efficiency but is more flexible, more durable, and, except in very small units, lower in first cost. A complete installation is shown in Fig. 131.

417. The Kelly press. This filter is of the intermittent pressure type. The standard press is shown in Figs. 132 and 133. The essential parts of the press are the supporting frame (1), the pressure tank, or press shell (2), the filter carriage (3), the basket of filter leaves (4), and the locking head mechanism (5).

The pressure tank is of steel, — the rear end dished, the front end open and carrying a heavy cast-iron flange or ring. To the

ring are attached heavy U bolts which engage the radial locking arms and close the press. The frame consists of two heavy I beams running along the sides of the shell, supporting that and the filter carriage. The front and rear ends of the filter carriage consist of supporting plates for the filter leaves, fastened together with channels. The front end of the carriage is attached to the cast-iron head; the rear end is mounted on wheels which travel on rails supported by brackets inside of the press shell. The entire carriage telescopes into the press shell, the head effectually closing the front end of the shell.

The filter leaves are rectangular in shape, running longitudinally in the filter frame. The filter leaves are made of steel

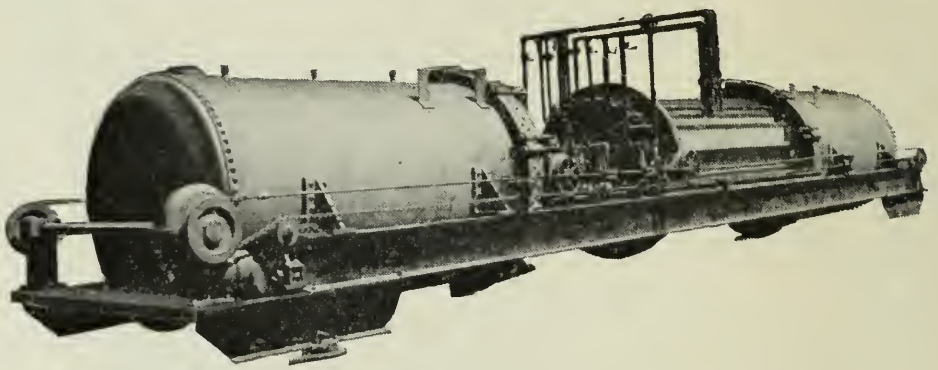


FIG. 133. Kelly filter press

pipe, pierced with a number of holes for the escape of the filtrate. A 4-mesh wire screen is spot-welded to the pipe frame so as to keep the filter bag from collapsing under the pressure and obstructing the flow of filtrate. The frame is covered with a special canvas bag which forms the filter medium. When the press is closed and pulp is forced into the shell under a pressure of from 30 to 60 pounds per square inch, a cake forms on the filter leaves. The filtrate passes through the canvas into the pipe frame, which is connected with the head of the press by means of a close nipple and quick-operating union. A defective leaf may be taken out and another substituted in a short time. Each filter leaf has a separate discharge, so that if one leaf fails it can be shut off until it is possible to make repairs.

The head-locking device consists of radial lever arms, the inner ends pivoted to a movable collar propelled along a central shaft by a toggle. The outer ends engage the U bolts, forcing

the head into a groove on the ring, against a gasket, thus insuring a perfect air-tight and water-tight joint.

The cycle of operation is as follows: The press is closed and locked, and the pulp is forced in through valve *b* (it is necessary to open valve *a* to allow air to escape). When the press is full of pulp, valve *a* is closed and the pressure (from 30 to 60 pounds per square inch) is maintained until the cake has built up on the leaves. This can be determined only by experiment. The formation period should be of such duration that the cake does not quite meet between the leaves, allowing a small space for the passage of the washing solution. This period will vary from two to six minutes. The excess pulp is then drained off, the press is filled with water or cyanide solution, and the cake is washed under pressure. The press is then opened by running out the carriage, and the cake can be discharged by washing it off with a stream of water, by vibrating the filter leaves, or by inflating the bags.

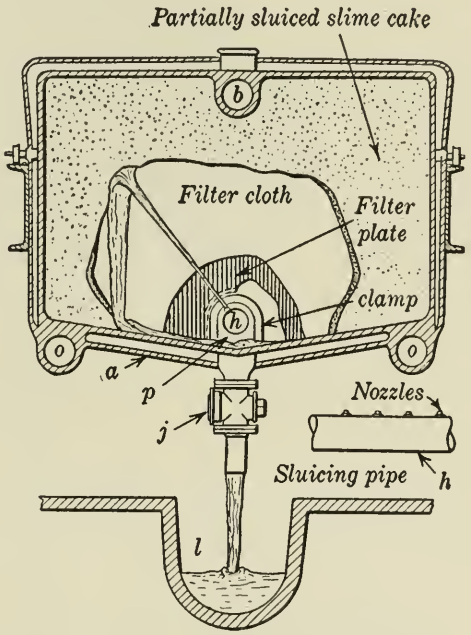


FIG. 134. Merrill slime filter frame

418. The Merrill press. The Merrill press is a pressure-type filter. It consists of a heavy frame carrying from 20 to 90 filter leaves. These leaves are alternately corrugated plates and hollow frames, as indicated in Figs. 134 and 135. The corrugated plates are covered with filter cloth. The entire press is tightly clamped by means of a hydraulic jack located at one end. The pulp to be filtered is forced into the press under pressure through passage *b*. The cake builds up on the canvas; the filtrate passes through and is collected by means of the corrugated plates. When a cake of sufficient thickness has formed, the press can be emptied and a barren solution or water forced through for a few minutes to displace the soluble gold. Then the press is ready for discharging. It differs from the ordinary plate-and-frame press in that it can be discharged without being opened — a long and tedious operation.

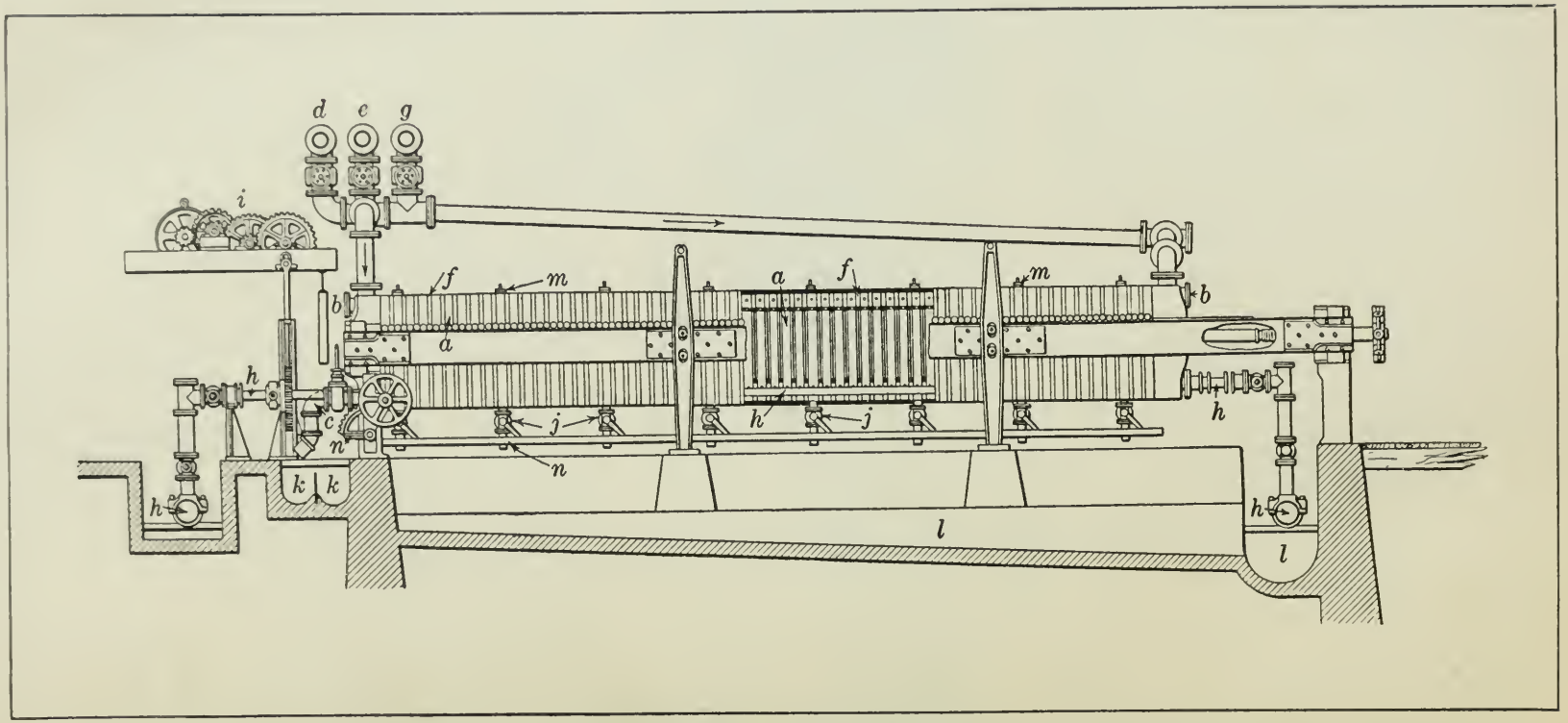


FIG. 135. Merrill slime filter

In the passage p which runs the entire length of the press is a 3-inch pipe h. Projecting from this pipe (one for each frame) are

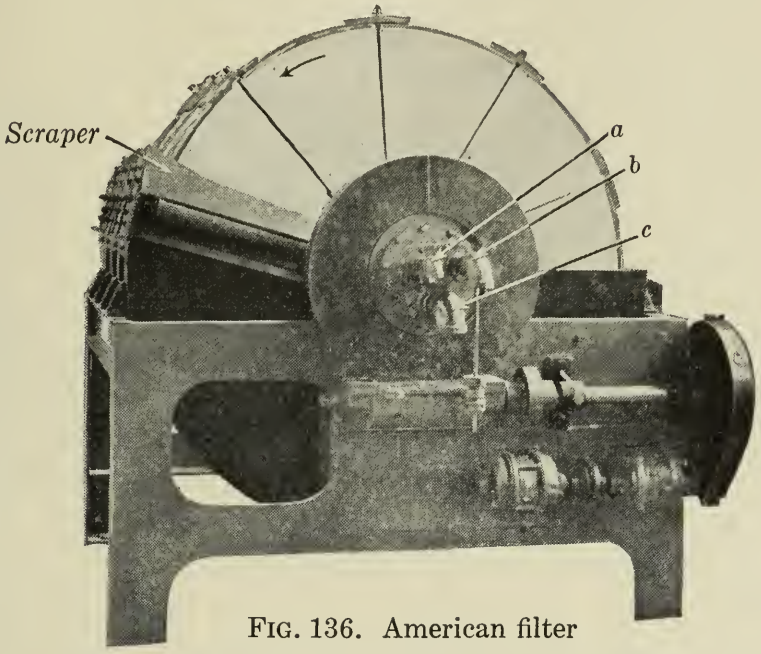


FIG. 136. American filter

a, low-pressure air; *b*, wash-water outlet; *c*, filtrate outlet

nozzles, so that high-pressure water may be discharged against the cake, thus washing it out of the frame. In order to do this as completely as possible, provision is made for revolving the pipe through an angle of 180 degrees, so as to reach every part of the frame. The slime is washed out through the discharge valve in the bottom of the frame.

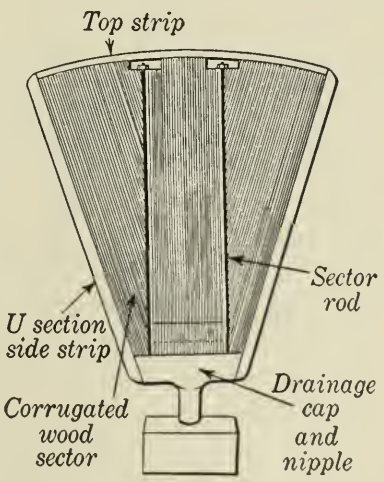


FIG. 137. Uncovered sector

419. The American filter. This filter, shown in Figs. 136 and 137, is of the continuous vacuum type. It consists of a horizontal hollow shaft with three or more filter disks, each about 8 feet in diameter. Each disk is made up of eight pie-shaped sectors connected by means of the hollow shaft with an automatic valve which controls vacuum, washing, drying, and discharging. The filter tank is divided, on the discharge side, into individual compartments, one for each filter disk. The sectors

are constructed of redwood and are deeply corrugated on both sides to permit free circulation of the filtrate. They are connected with the main shaft by means of easily operated nipples. The actual filter medium is a special bag of twill or canvas so constructed that it can be slipped over the end of the sector, clamped in place at the periphery, and wrapped with cord at the nipple, which is thus effectually sealed. At the discharge side there are scrapers to remove the cake into the discharge pans.

In operation the tank is filled with pulp, and the vacuum is applied to the slowly revolving filter. The cake forms on both sides of the leaves, and the liquid passes out through the automatic valve. Shortly after the disk emerges from the pulp a spraying device applies cyanide solution and then wash water to the cake; then air drawn through the cake carries with it some moisture, and finally a puff of compressed air dislodges the cake just before it reaches the scraper.

Several advantages are claimed for this type of filter: (1) It has a larger capacity per cubic foot of plant space; (2) it requires a smaller amount of head room; (3) by dividing the tank into several compartments a single filter may handle several different kinds of feed simultaneously; (4) the sectors may be easily removed for repairs without shutting down the filter for more than a few minutes.

420. The Dorrco filter. This filter has many original and apparently very desirable features. It is a continuous vacuum filter of the rotary-drum type, with the filtering medium on the *inside* of the drum. The general construction of this filter is shown in Figs. 138 and 139. The drum, which acts as the pulp-container, is closed at one end, the other end being open for the discharge of the filter cake and to permit observation of the filtering operation. The filtering medium (of canvas) is divided into a number of panels so constructed that any one may be quickly removed for repairs. The drum is mounted on a trunnion bearing at the closed end and is supported at the open end by riding rolls. Additional support is provided for the discharge-cake conveyor which runs through the center of the drum. Vacuum and pressure pipes are attached to the outside of the drum and connected, by means of a rotating valve, with sources of vacuum and pressure. The filter is driven in a clockwise direction by a worm gear. The feed is brought into the drum

through a pipe, and as the drum revolves the cake forms and is dewatered. When it reaches the discharge point, near the top of the drum, low-pressure air is admitted through the

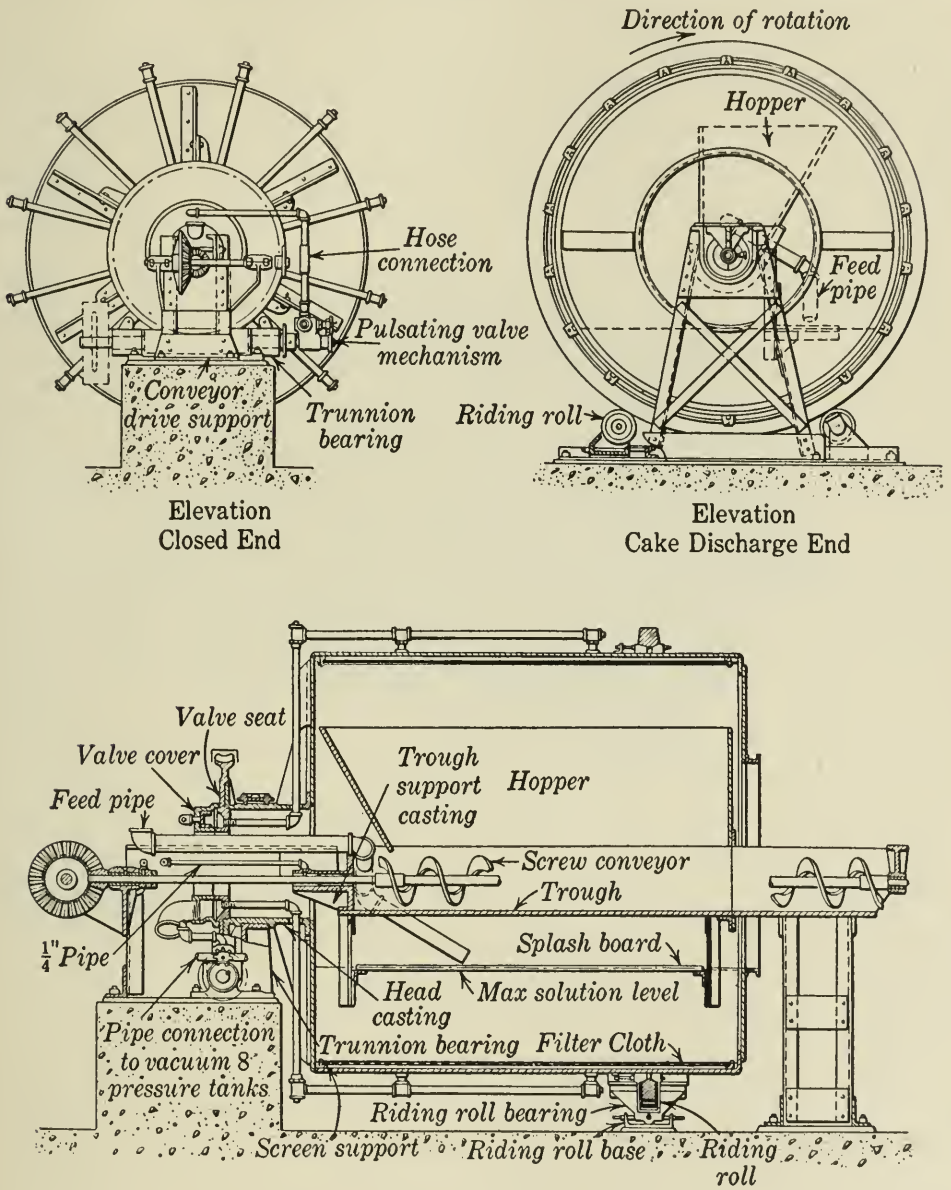


FIG. 138. Dorrco filter press

automatic valve; this causes the cake to fall freely into the hopper from which it may be removed by a screw or belt conveyor.

This filter has many advantages. Since the drum acts as a pulp-container, the force of gravity acts to assist filtration. As

the feed enters the drum the coarser particles have a tendency to settle onto the cloth, thereby assisting in forming the cake. This layer of coarse particles against the filter cloth serves as an additional filtering medium for the fine particles and prevents them from entering the pores of the cloth, thus increasing the effectiveness of the filter and prolonging the life of the cloth. Gravity also assists in cake discharge; and here again, since the fines do not come in direct contact with the cloth, the cake does not have a tendency to stick, but discharges freely. Although

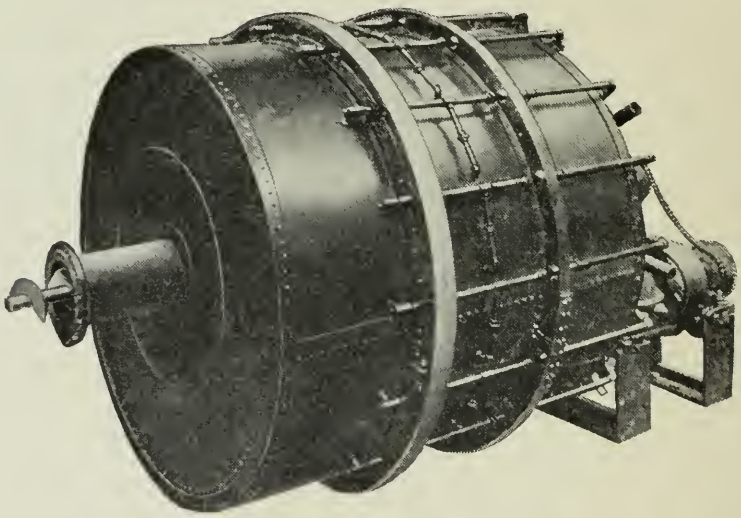


FIG. 139. The Dorrco filter

it has been on the market for only a short time, this filter has shown that it can adapt itself to variations in pulp consistency better than any other. After a shut-down it can be started up much more easily than the outside-fed type.

421. The choice of a filter. This will be governed entirely by the character of the ore and by local conditions. No single filter is a panacea for all our filtration ills. For large installations, handling pulp at ordinary temperatures, the suction type of filter is very economical and has a large capacity. It will not work well with hot solutions, owing to the vapor generated under a vacuum, nor will it give complete satisfaction with ores containing high percentages of clay or colloidal material. With such material the cake is thin, the capacity is correspondingly decreased, and the moisture in the cake is considerably higher than could be obtained with pressure filters.

The pressure presses, such as the Kelly and the Merrill, are undoubtedly more expensive to operate than the suction filters. They consume large quantities of compressed air, which calls for a considerable investment in machinery. The filter medium is subject to more intensive service, and the press, being intermittent in action, has a much smaller capacity per cubic foot of plant space than other types. On the other hand, with the high pressures available (up to 100 pounds per square inch) the most stubborn pulp can be filtered, washed, and dried. They are especially adapted to the handling of hot solutions.

422. Acid wash. In handling cyanide pulps, compounds of Ca, Al, and Zn deposit on the canvas of the presses. The degree of this deposition will of course vary with different ores and schemes of treatment. In ordinary operation the filter cycle remains normal for about three weeks after the canvases are installed. Then the cycle, particularly cake formation, must be lengthened gradually as this deposit forms, until at the end of six weeks the cycle may be 50 per cent longer. The filter medium is then treated with a 0.9 per cent HCl solution for about one hour. This solution will dissolve a part of the deposit and dislodge the rest, bringing the cycle back nearly to normal. It will, however, weaken the fabric and shorten the life of the leaf. Sometimes it is possible and advisable to give the press two or even three acid washes, but usually the canvas grows very weak, and many of the leaves become torn and must be taken out of service.

Precipitation

423. Clarification. Whatever method of precipitation is used, the solution must be absolutely clear and free from suspended matter. Any slime would be collected with the gold and would result in a loss of metal in the refining operation, high cost of this operation, and low-grade bullion. Even under the best conditions, and with the most careful operation, slime will get through into the filtrate from either the leaching process, the filtration process, or the decantation process. Broken filters, torn cloths, and careless workmen can never be avoided. It is therefore always advisable to interpose between the main filtration plant and the precipitation plant a secondary, or clarification, unit. These presses or tanks, as the case may be, will rid

the pregnant solution of the last traces of slime and suspended matter and will deliver a crystal-clear filtrate for precipitation.

The simplest clarifying device is a sand filter or filters. These are usually circular tanks about 30 feet in diameter and 4 feet deep, with a filter bottom similar to that used in sand-leaching tanks. This bottom is covered with about 6 inches of clean sand, about 30-mesh in size. The slime will collect on top of the sand in the form of a thin film. If the presses are in good condition, the life of the bed will be several days or weeks. In time, however, filtration will slow up, and it is then necessary only to drain the tank, skim off about one quarter of an inch of the top, and start up again. The sand which has been removed can be washed, dried, and used again. The disadvantage of such an installation, particularly in large plants, is that the tanks occupy a large amount of valuable plant space and are expensive to construct.

Of the filter presses used for clarification the Merrill is probably the best, for, with pressure, very large amounts of solution can be handled and the press may be cleaned without being opened. In handling cyanide solution, as with the primary presses, the canvases become covered with a deposit of basic salts of Ca and Al, so that it is necessary to give them an acid wash from time to time.

424. Precipitation with zinc. Zinc, in the form of either shavings or dust, is almost universally used today for the recovery of the gold and silver from the cyanide solution. The reaction between the zinc and the pregnant solution is represented by the following equation:

$$KAu(CN)_2 + 2\,KCN + Zn + H_2O = K_2Zn(CN)_4 + Au + H + KOH.$$

The solution to be precipitated should contain not less than 0.03 per cent of KCN; if the percentage is lower than this, it must be brought up to strength.

It has been found that the addition of lead-acetate solution is of material aid in precipitating solutions containing Cu or those which tend to form white precipitate. The zinc shavings are dipped in a 10 per cent solution of lead acetate. After from four to six days of contact with the solution, precipitation becomes sluggish. The shavings are then taken out and replaced by new, and the old ones are reactivated with fresh acetate.

425. The zinc box. A zinc box, shown in Fig. 140, contains from five to nine compartments, each about 2 feet square. It should be made of steel and painted at frequent intervals with some heavy paint like P & B mixture. Each compartment has a false bottom of woven-wire screen or of punched plate to allow free circulation of the solution and to hold the zinc shavings in place. A fine, threadlike shaving is to be preferred to the ribbon form. It should be such as to give a maximum surface

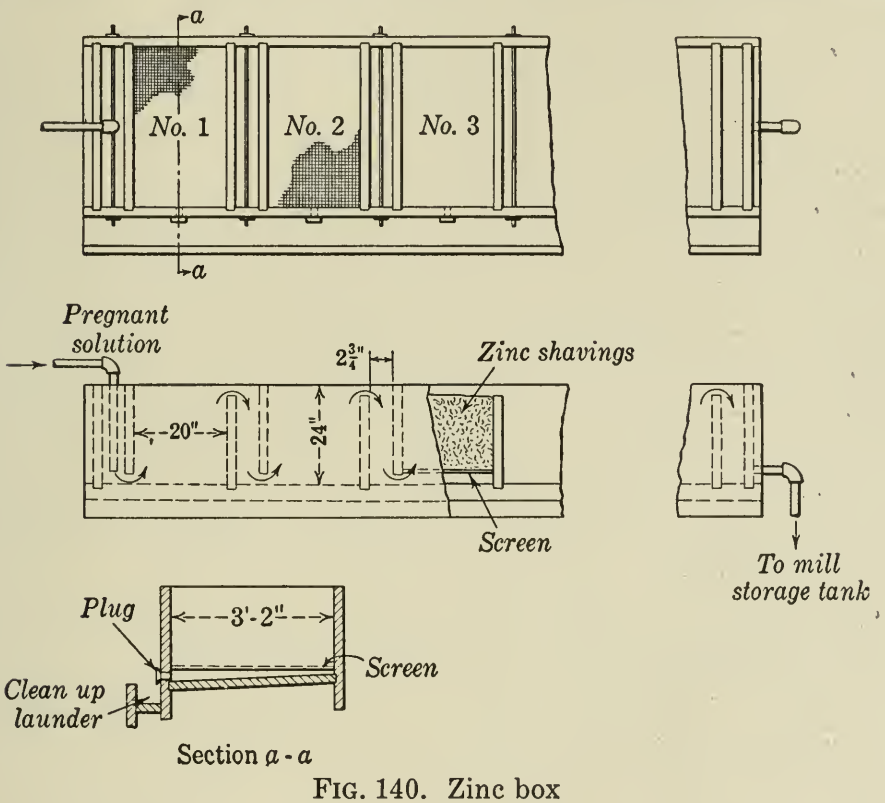


FIG. 140. Zinc box

per unit of weight without being so fragile as to break into fine pieces. A width of $\frac{1}{500}$ inch is perhaps the most efficient. The zinc shavings are packed in so as to fill the compartment almost to the top. As indicated in the section, the compartments are in cascade, and the partitions between the zinc boxes are so arranged that the flow through the boxes is by gravity, the cyanide solution passing up through the zinc. The last compartment is often left empty in order that it may act as a settler for the precipitated gold. Each compartment is provided with an outlet pipe for removing the solution and collecting the precipitated gold at clean-up time. Usually two series of

boxes are provided, so that one can be in use while the other is being cleaned. Sometimes, in large plants, there is one for strong solution and one for weak. Both the boxes and the connecting launders should be provided with locked covers in order to prevent theft of the precipitate. As a general rule most of the gold is precipitated in the first three compartments. As the zinc in the compartment is dissolved, zinc from the lower compartments is transferred to keep the first full, and fresh zinc is added to the lower compartments. This serves still further to concentrate the gold in the first compartments and to reduce the loss of the metal at clean-up time. This dressing of the boxes takes place every six to ten days, depending upon the richness of the solution.

426. Conditions for efficient precipitation. One great trouble in zinc-box precipitation is the formation of a white precipitate which coats the zinc and seriously interferes with the precipitation of the precious metals. It consists of zinc hydroxide, zinc cyanide, and zinc potassium ferrocyanide. Its origin is rather obscure. The absence of sufficient free alkali or cyanide and the exposure of the zinc shavings to the air seem to promote its deposition. Another trouble is the precipitation of Cu. This covers the zinc and prevents further action with the gold-bearing solution.

According to Clennell the principal conditions for efficient zinc-box precipitation are as follows: (1) freedom of the entering solution from solid matter in suspension, (2) the presence of a sufficient amount of free cyanide, (3) the presence of sufficient free alkali, (4) the absence of an excessive amount of foreign salts, particularly of Cu and Fe, (5) a regular and uniform flow through the boxes, (6) a sufficient volume of zinc per ton of solution precipitated, (7) a clean, unoxidized surface of zinc so that the gold, once deposited, may be easily detached and collected.

427. Clean-up. This takes place either once or twice in a month, depending upon the richness of the ore. The flow of solution to the box is stopped, and water is run in to displace the cyanide and prevent any re-solution of the gold. The zinc shavings are lifted out by hand from the first compartment, each handful being agitated in the water so as to dislodge the precipitated gold. This settles through the screen to the bottom

of the compartment and may be removed through the plug. The plug is replaced, the compartment is filled with water, and the zinc is again carefully washed and rubbed. Two or three such washings will remove all the gold. The spent zinc is placed to one side to be used for refilling the box. The succeeding compartments are cleaned in a similar manner, and the precipitate from all of them is collected in an acid tank, or clean-up sump. The contents of this tank are allowed to settle, the supernatant liquid is siphoned off, and the remaining liquid is passed through a filter press to recover the gold. The precipitate is dried and treated by one of the methods later described under "Refining." When the zinc box is refilled, zinc from the second compartment is used to make up any deficiency in the first, all the spent zinc is moved up, and fresh zinc is added only to the last compartment.

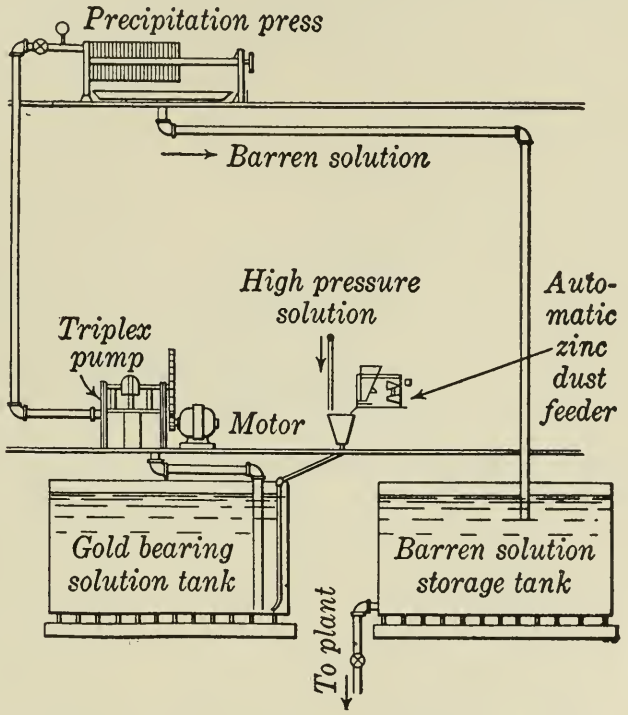


FIG. 141. Merrill precipitation process

428. The Merrill precipitation process. In the zinc-box precipitation process a great deal of trouble is experienced with the formation of the white precipitate and the deposition of copper upon the zinc, rendering the clean-up long and laborious as compared with the Merrill process. This process is shown in diagrammatic form in Fig. 141. It consists of the addition of very finely divided zinc (dust) to the pregnant solution and the recovery of the precipitated gold or silver by means of a specially constructed filter press. The solution containing the gold and silver is collected in the lower tank. Mounted above this tank, with its suction extending to the bottom, is a triplex pump. An emulsion of zinc dust and cyanide solution is delivered by

an automatic zinc-dust feeder to the mouth of the suction pipe, and precipitation of the precious metals takes place almost instantly. There is no opportunity for the zinc to become covered with either copper or the white precipitate. The solution is then pumped to the precipitation presses, where the gold collects in the frames and the clear solution is discharged into the solution storage tank.

The preparation of the emulsion of zinc dust and the addition of this to the solution in the tank requires careful supervision. The zinc may be added by means of a small belt or screw conveyor with suitable arrangements for varying the rate of feed, but the best method is indicated in Fig. 142. It consists of a hopper *a* for holding the zinc dust, from which, by means of an adjustable screw feed *b*, the zinc dust is fed into the mixing cone *c*. There it meets a stream of solution issuing from the pipe *d*. By means of a float valve the solution can be kept at such a height as to submerge the discharge of the smaller cone. Finely divided zinc dust tends to float on the solution, and it is only by emulsifying it in this way that efficient precipitation is obtained. The rate of feeding is closely observed from time to time, so that sufficient zinc dust will be added to precipitate all of the precious metals and yet not so much as to lower the grade of the bullion.

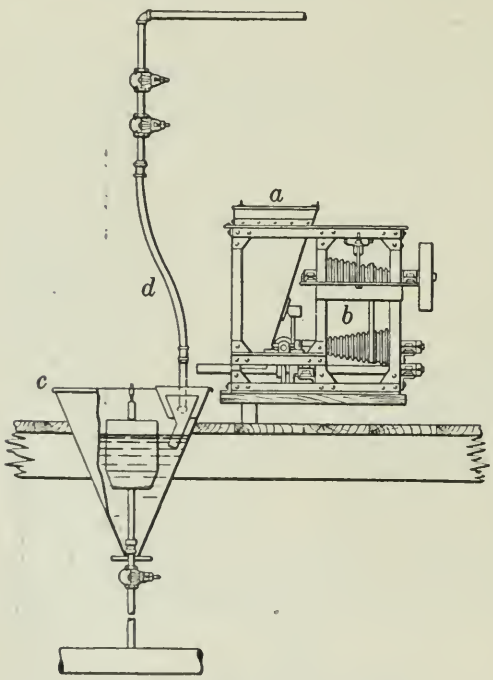


FIG. 142. Zinc-dust feeder

Clean-up is much more easily accomplished than with the zinc boxes. The flow from the solution tank is diverted to a spare press, the one which has been in use is drained and blown with compressed air to dry the cake so that it may be more easily handled, and the press is opened. If the cycle has been properly gauged, the filter press will be nearly full of precipitated gold and zinc dust. This material is scraped out into a

suitable container, the canvas is removed and burned, and the ash is added to the rest of the precipitate. New canvases are then put on, and the press is closed and made ready to be put in operation again. The precipitate is refined by the usual methods.

429. Crowe process. The process of precipitating precious metals from cyanide solutions is one of reduction, and hence it follows that oxidizing conditions will make it less efficient; such conditions exist in the ordinary cyanide solution. Owing to the intense aëration in the agitation process the mill solution is saturated with air (23 per cent O). The Crowe process, shown in diagrammatic form in Fig. 143, consists of the removal of most of this air just previous to precipitation. The apparatus consists of a receiver, or drum, about 4 feet in diameter and 10 feet high, filled with a latticework of redwood strips from a point about 18 inches above the bottom to a point 2 feet from the top. This latticework serves to break up the falling solution, form a thin film over the strips, and thus promote more efficient de-aëration. The solution to be precipitated may come from a tank set 24 feet above the top of the receiver. This permits a more nearly constant flow through the machine than could be obtained with a pump, as shown in the illustration. A vacuum pump maintains as nearly perfect vacuum as possible in the receiver and thoroughly de-aërates the falling solution. A pump to take away the de-aërated solution is set at a distance below the receiver corresponding to the barometric pressure at that point. It should be such that the foot valves of the pump are covered and no air is drawn in. The solution level in the bottom of the receiver is controlled by means of a float connected with a valve in the intake pipe. The zinc

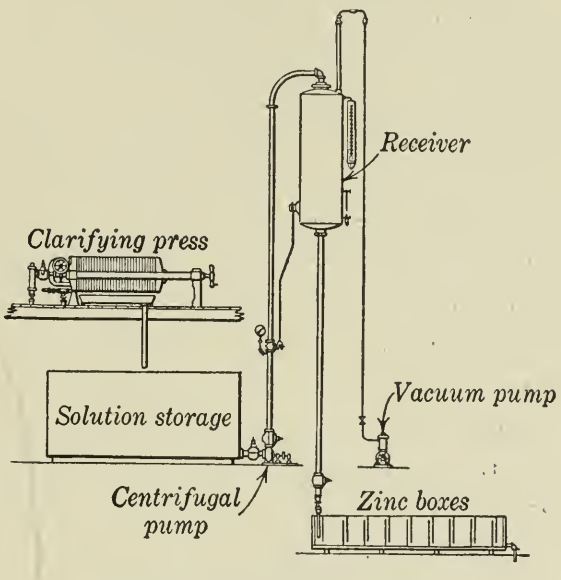


FIG. 143. Crowe process

dust for precipitation is introduced into the suction of the lower pump, which sends it on to the precipitation press.

The advantages claimed for this process are as follows: (1) it reduces the zinc consumption from 30 to 40 per cent; (2) it increases the capacity of the existing plant at least 40 per cent; (3) it eliminates all trouble with white precipitate even in the coldest weather; (4) it reduces clean-up labor and refining expense.

Refining the Precipitate

430. Drying. The precipitate from the press usually contains about 40 per cent of moisture. It is transferred to drying pans about 2 feet by 4 feet and 4 inches deep. These pans are then heated in an electric drier or a muffle furnace until the last trace of moisture has been driven off. The precipitate must be handled very carefully to avoid excessive loss, for it is light and dusty. The dried precipitate may be treated in a variety of ways, the choice depending upon the richness of the product and the presence of certain impurities. The most important are (1) direct fusion, (2) fusion after roasting, and (3) treatment with HCl or H_2SO_4 with subsequent fusion.

431. Direct fusion. The dried precipitate is mixed with borax, sodium carbonate, niter, and silica, the relative proportions of these depending upon the composition of the precipitate. This mixture is placed in a graphite crucible and carefully melted down. After a quiet fusion has been obtained the metal is poured out into molds and allowed to solidify, and the slag is broken away from the precious metal. This slag contains considerable gold and silver; so it must be returned to the process for re-treatment. This method of refining the precipitate is applicable only to high-grade bullion; those containing much Zn, Pb, or Cu must be treated by one of the other methods.

432. Roasting and fusion. Impure precipitates, especially those containing very much Zn, are best treated by this method. The dried precipitate, sometimes mixed with niter to intensify the oxidizing action, is placed in iron pans about 2 feet by 4 feet and 4 inches deep, and heated in a muffle furnace to a dull red heat. All the Zn is thus volatilized, and the roasted product is mixed with the proper fluxes as in the previous method and melted down in a crucible furnace to bullion and slag.

433. Acid treatment. This method is in more extensive use than either of the other two methods, for most of our bullions are too impure to be treated by simple fusion and contain too much Cu to be treated by roasting and fusion. None of the copper is eliminated in the roasting process, and while subsequent fusion would slag a small portion of the oxidized metal, most of it would be found in the bullion. Before the precipitate is dried it is placed in a wooden or lead-lined vat with H_2SO_4 in order to dissolve out as much of the base metals as possible. A stirrer is provided for agitating the contents of the vat, and at some plants the pulp is heated by means of steam jackets. These vats should be provided with tight-fitting covers with small doors for the charging of the precipitate and with hoods for the escape of the fumes. When the action has ceased, the vat is filled with water, the precipitate is allowed to settle, and the supernatant liquor is siphoned off. After two or three washings the pulp is pumped through a filter press and the cake is dried, roasted, and melted as in method 2.

Refining the Bullion

434. General. The bullion from stamp milling or cyaniding is usually impure, ranging in fineness from 750 to 985, the gold and silver being alloyed with Cu, Zn, Pb, and other base metals. The methods of refining in common use today are (1) parting with H_2SO_4, (2) parting with HNO_3, (3) parting by electrolysis, (4) parting with chlorine.

435. Parting with H_2SO_4. In order to part successfully by this method the bullion should contain at least two and one-half parts of silver to one of gold. If it contains less than this, low-grade bullion or silver must be added in order to maintain this ratio. The bullion should not contain more than about 10 per cent Cu. It is melted and cast into flat ingots, similar in shape to the "buckles" of lead used in the manufacture of white lead, each buckle containing a few ounces of bullion. These are then parted in a cast-iron kettle with H_2SO_4 (1.82 specific gravity). Care must be taken to dispose of the fumes by means of a hood and effective ventilation. When all action has apparently ceased, the contents of the kettle are allowed to settle and the supernatant liquid is decanted off into a lead-lined receiving

tank. It may be necessary, with impure bullions, to treat the residue several times with fresh acid. The gold residue is washed several times with hot water and filtered, and the cake is dried, fused with suitable fluxes, and cast into ingots. The silver is precipitated from the acid solution by means of copper plates, the reaction involved being

$$Ag_2SO_4 + Cu = CuSO_4 + 2\,Ag.$$

When all the silver has been precipitated, it is washed several times with hot water in order to remove the copper sulphate, and is then collected, dried, melted, and cast into ingots. The copper sulphate commands a ready market and may be recovered by repeated crystallizations.

436. Parting with HNO_3. This method is not in common use, for HNO_3 is much more expensive than H_2SO_4. For the best work there should be at least two parts of Ag to one of Au, but the process may be carried out with as low as one and three-fourths parts. The bullion is melted and granulated by being poured into cold running water. These granules are then charged with one and one-half times their weight of HNO_3 (specific gravity 1.2) into porcelain or stoneware vessels. These are heated by steam and the contents kept hot for about four hours; at the end of that time most of the silver will be dissolved. The contents are allowed to settle, the clear liquor is siphoned off and diluted with water to prevent crystallization of the silver nitrate. There may be one or more additional treatments with acid in order to dissolve the last of the silver. The gold residue is washed with water, dried, melted, and cast in the usual way.

The silver may be recovered from the solution by precipitation as the chloride. This chloride is transferred to treatment vats, where it is reduced to metallic silver by means of zinc and dilute sulphuric acid. This reduced silver is washed repeatedly with hot water, filtered off, dried, melted, and cast into ingots.

437. Electrolytic refining. This is the method in general use in the mints of the United States. The scheme of treatment will depend entirely upon the gold content of the bullion. That which is 900 fine in gold or purer is refined by method 1. Low-grade gold bullion and silver bullion are melted together to produce a bullion running about 600 fine in silver, and this is refined by method 2.

In method 1 the anodes are of gold bullion (900 fine in Au and about 75 fine in Ag) measuring $3\frac{1}{2}$ inches wide, 9 inches high, and $\frac{1}{2}$ inch thick. The cathodes are thin sheets of pure gold suspended in an electrolyte of gold trichloride containing 7 per cent of Au and from 10 to 12 per cent of free HCl. The containers are porcelain or earthenware jars, and the electrolysis is carried on at a relatively high-current density of 90 amperes per square foot.

Method 2 is the most common, for there are few plants producing bullion of as high a grade as that required for method 1. In this the anodes, of about the same size as that used in the refining of gold bullion, are 600 fine in silver. They are suspended in earthenware jars with thin sheets of pure silver as cathodes. The electrolyte is a solution of $AgNO_3$, carrying about 3 per cent of Ag and from $1\frac{1}{2}$ to $2\frac{1}{2}$ per cent of free HNO_3. The current density is 0.8 ampere per square foot. In the electrolysis pure silver deposits on the cathode, while a slime or mud of gold collects in the bottom of the tank and on the surface of the anodes. This slime is collected from time to time, melted, and cast into ingots.

438. Parting with chlorine. This process depends upon the fact that if chlorine gas is passed through molten bullion the gold remains unaffected, while any silver present is converted into fusible chloride which floats on top of the gold, and any Pb, Cu, Sb, etc. is converted into volatile chlorides. The process is carried out as follows: The gold bullion is melted down in a crucible of white clay, — $10\frac{1}{2} \times 5$ inches, — contained in a larger "guard" pot of graphite. The smaller crucible is covered with a lid, perforated with two holes for the insertion of $\frac{1}{8}$-inch clay pipes through which the chlorine gas is introduced. The chlorine is generated from HCl and MnO_2, and the flow so adjusted that it all combines with the silver and base metals, no bubbling taking place. When the gold is sufficiently purified, the supply of chlorine is shut off, the clay pot is removed from the furnace, the gold is allowed to solidify, and the molten silver chloride is poured out into a mold. The silver may be recovered as the pure metal by reduction with copper in acidulated water that is kept boiling.

439. Chemistry of the cyanide process. According to Elsner the reaction which takes place when crushed ore containing

finely divided gold is brought in contact with a solution containing from 0.1 to 0.5 per cent of cyanide is represented by the following equation:

$$2\,Au + 4\,KCN + O + H_2O = 2\,AuK(CN)_2 + 2\,KOH.$$

Oxygen is indispensable for the reaction, although it is uncertain whether its action is a direct one. It follows that efficient solution of the gold requires thorough agitation of the pulp. The addition of chemical oxidizing agents such as permanganate, peroxide, or ozone, on the other hand, is of doubtful benefit and has not been attended with much success. The use of bromocyanide (BrCN) will be described later.

The amount of cyanide actually used up in dissolving the gold in the average ore is almost negligible as compared with the actual cyanide consumption. It will be noted that the equation given above calls for only 0.66 unit of KCN for each unit of Au, while in practice the consumption is from twenty to forty to one (normally 1.0 pound of cyanide per ton of ore). The excess must be accounted for in some other way than by the solution of the precious metals. This loss takes place in a number of ways; the most important are (1) loss in precipitation, (2) mechanical loss, (3) combination with base metals, (4) combination with iron.

There is a considerable loss of cyanide in precipitating gold from cyanide solution with zinc:

$$KAu(CN)_2 + 2\,KCN + Zn + H_2O = K_2Zn(CN)_4 + Au + KOH + H.$$

Cyanide is also used by direct combination with zinc as follows:

$$Zn + 4\,KCN + 2\,H_2O = K_2Zn(CN)_4 + 2\,KOH + H_2.$$

There is always a loss in cyanide in the residue. In good practice this will range from $\frac{1}{4}$ to $\frac{1}{2}$ pound per ton of ore. It would be possible to wash out the last trace of cyanide from the tailings, but it would not be economical, owing to the difficulty of handling and disposing of such a large bulk of solution. The loss will depend upon the strength of the mill solution, the percentage of moisture in the residue, and the method of dewatering.

Pyrite, when exposed to the action of the air or certain oxidizing solutions, decomposes according to the following equation:

$$3\ FeS_2 + 2\ H_2O + 11\ O_2 = FeSO_4 + Fe_2(SO_4)_3 + 2\ H_2SO_4.$$

Both ferric sulphate and sulphuric acid are "cyanicides" and decompose the cyanide. Unless removed or neutralized they will cause a very high consumption of the reagent. Either caustic soda or lime (usually the latter, since it is cheap and easily obtained) is used to neutralize the acidity of such an ore. Usually an additional amount over and above that immediately necessary is added to provide for further decomposition. The amount added, expressed in pounds of CaO per ton of ore, is termed *protective alkalinity*. The action of the lime in neutralizing the decomposition products is expressed by the following equations:

$$FeSO_4 + Ca(OH)_2 = Fe(OH)_2 + CaSO_4.$$
$$H_2SO_4 + Ca(OH)_2 = 2\ H_2O + CaSO_4.$$
$$Fe_2(SO_4)_3 + 3\ Ca(OH)_2 = 2\ Fe(OH)_3 + 3\ CaSO_4.$$

When insufficient free alkali is present, CO_2 may decompose cyanide according to the following equation:

$$KCN + CO_2 + H_2O = HCN + KHCO_3.$$

All base metals in the ore which are soluble in cyanide also cause a consumption of the reagent, Cu and Fe being the most common:

$$2\ Cu + 4\ KCN + 2\ H_2O = K_2Cu_2(CN)_4 + 2\ KOH + H_2.$$
$$Fe + 6\ KCN + 2\ H_2O = K_4Fe(CN)_6 + 2\ KOH + H_2.$$

440. The bromocyanide process. This process is used with two classes of refractory ores: (1) ores requiring a more rapid solution of the gold than is possible by the straight cyanide process, so that excessive cyanide consumption through the action of cyanicides is avoided; (2) ores containing tellurides of gold and silver not dissolved by an ordinary cyanide solution.

The bromocyanide is prepared from the bromide and bromate according to the following reaction:

$$2\ NaBr + NaBrO_3 + 3\ NaCN + 3\ H_2SO_4 = 3\ BrCN + 3\ Na_2SO_4 + 3\ H_2O.$$

The solution of the gold is represented by the following reaction:

$$BrCN + 3\ NaCN + 2\ Au = 2\ NaAu(CN)_2 + NaBr.$$

This process, owing to the fact that it is both expensive and delicate, is used only on certain very refractory ores in Colorado, California, and Australia. The amount of free alkali must be much less than in the straight cyanide process. The bromocyanide decomposes rapidly and also induces decomposition of the NaCN.

THE UNITED EASTERN MILL*

441. Crushing and grinding. This plant is a good example of a simple, compact mill employing countercurrent decantation. The company is engaged in treating about 300 tons per day of an ore consisting of a mixture of quartz and calcite and containing about $20 per ton in gold and silver. The silver-gold ratio is about one to two by weight. A flow sheet of the plant is shown in Fig. 144. The ore is screened at the bin over 2-inch grizzlies into a fine and a coarse product. The coarse product passes through a No. 6 Tellsmith crusher set to crush to 2 inches. The fine product from the bin joins the discharge of this crusher, and both pass over a Merrick weightometer into the mill bin. The ore is then ground in two No. 64½ Marcy mills working in closed circuit with Simplex Dorr classifiers. The extent of grinding is indicated in Table XLIII.

TABLE XLIII. SCREEN ANALYSES IN COARSE AND FINE GRINDING

MESH	MARCY DISCHARGE	CLASSIFIER SANDS	CLASSIFIER OVERFLOW	BALL-PEB DISCHARGE	CLASSIFIER SANDS	CLASSIFIER OVERFLOW	CONE OVERFLOW
+ 4	1.0	2.5					
+ 6	2.5	9.5					
+ 8	7.5	19.0					
+ 10	16.0	35.0					
+ 14	28.0	54.0					
+ 20	37.0	67.0	4.0				
+ 30	54.0	81.0	19.0				
+ 48	61.0	85.0	28.0	4.07	5.43		
+ 65	66.0	88.0	37.0	11.12	13.71		
+ 100	70.0	89.5	44.0	24.18	30.00		
+ 150	73.0	91.0	48.0	43.75	57.30	5.01	0.12
+ 200	77.0	93.0	66.0	63.75	81.40	23.55	7.08
− 200	23.0	7.0	34.0	36.25	18.60	76.45	92.92

* *Engineering and Mining Journal-Press*, March 14, 1925.

The overflow of the Simplex classifiers is distributed to three regrinding mills which are 5 × 6 foot Allis-Chalmers ball granulators. These mills work in closed circuit with a Duplex Dorr classifier. The pulp overflowing from the Dorr classifiers is maintained at a consistency of about five parts of solution

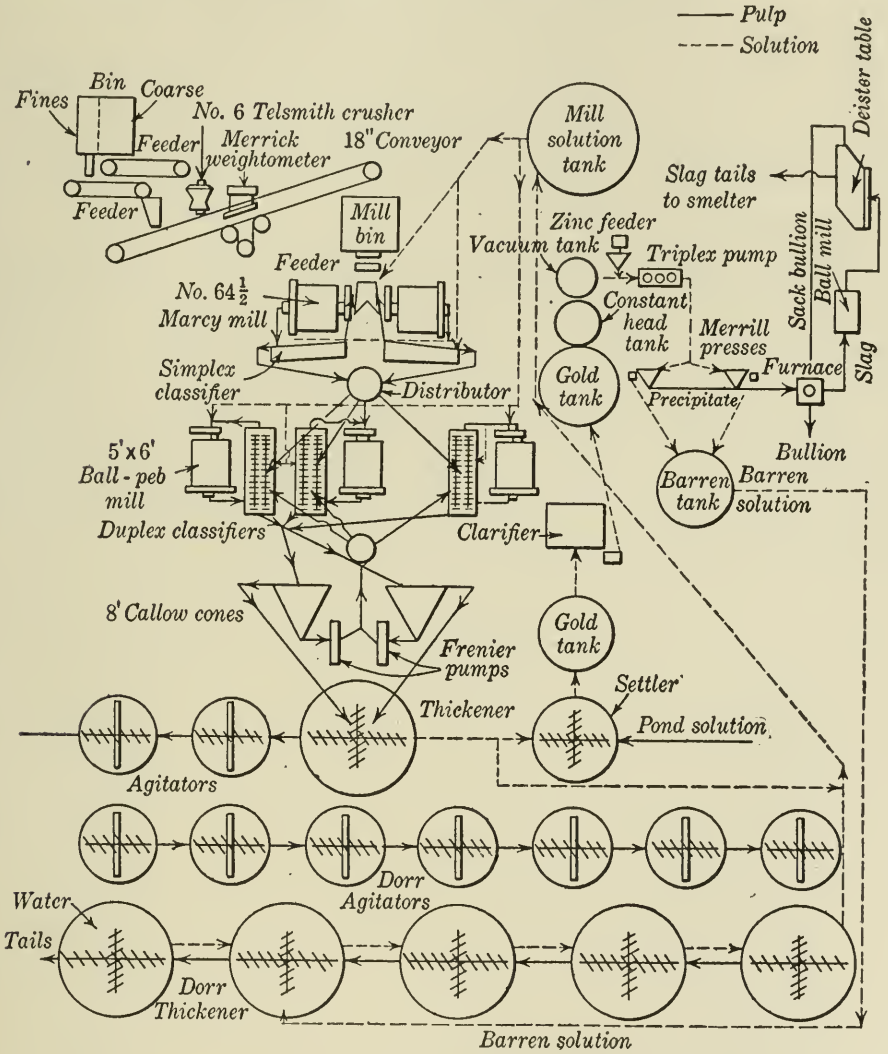


FIG. 144. Flow sheet of the United Eastern cyanide plant

to one part of solids. All grinding is carried out in cyanide solution. The pulp is then run to two Callow cones. The spigot of these Callow cones is returned to the classifier, while the overflow goes on to the cyanide plant. Under ordinary conditions the ore must be ground until 92 per cent of it will pass a 200-mesh screen. The overflow from the Callow cones has a consistency of about four and one-half parts of solution to one part of

solids, so that before agitation it must be thickened in Dorr thickeners to a consistency of one part of solution to one of solids.

442. Agitation. The spigot from the primary thickener is pumped by means of diaphragm pumps to nine Dorr agitators. The pulp from the last agitator flows by gravity to a second thickener, where it is thoroughly mixed with the overflow solution from the third thickener. The flow from the second thickener to the sixth, or final, thickener is countercurrent, fresh water being added to the last tank and barren solution to the one preceding. The cyanide solution is held at about 2.5 pounds of cyanide per ton of ore.

443. Precipitation. The solution overflow from the primary thickener runs to a sump, and thence to a Merrill clarifying filter. The clear solution then goes to the steady-head tank of a Crowe vacuum system. After de-aëration the gold and silver are precipitated by zinc dust in Merrill precipitation presses.

The extraction in this plant (on $19.80 heads) over a period of eight years averaged 96.59 per cent. The milling costs over the same period are indicated in Table XLIV.

TABLE XLIV. COST OF MILLING

	COST PER TON
General	$0.161
Lighting	0.005
Water	0.108
Crushing	0.055
Coarse grinding	0.356
Fine grinding	0.469
Cyaniding	0.523
Tailing disposal	0.025
Clarification	0.033
Precipitation	0.095
Refining	0.074
Sampling	0.003
Assaying	0.031
Heating	0.031
Miscellaneous	0.025
Total	$1.994

The costs given above, while accurate for this particular plant and scheme of treatment, serve only as a general indication of the cost of treatment for other ores. Individual costs will of course depend upon the physical and chemical characteristics of the ore in question.

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CHAPTER XI

SILVER

444. Physical properties. Silver is harder than gold, softer than copper, and very malleable and ductile. It is the whitest of all the metals and the best conductor of heat and electricity. The specific gravity of the cast metal is 10.5. The melting point of the pure metal is 960° C. and the boiling point about 1950° C., but the metal is volatile to some extent if heated very much above its melting point, and this volatility is very much increased by the presence of such impurities as Pb, Zn, As, and Sb. The tensile strength is about 36,000 pounds per square inch. When molten it will absorb up to twenty-two times its own volume of oxygen from the air.

445. Chemical properties. Nitric acid is the best solvent for silver, although it dissolves the metal somewhat slowly. It is soluble in boiling concentrated sulphuric acid but not in the dilute acid. Hydrochloric and other acids affect it very slowly. When in a fine state of subdivision it is slowly soluble in dilute solutions of sodium or potassium cyanide. Silver, at ordinary temperatures, is not acted upon by either dry or moist air. The familiar blackening of silver utensils is due to the formation of a film of Ag_2S from the small amount of H_2S gas present in the air when sulphur-bearing bituminous coal is being burned. Silver also dissolves in solutions of sodium hyposulphite with the formation of a double hyposulphite of Na and Ag. Metallic silver readily forms an amalgam with mercury. The chloride is also decomposed by mercury, but the sulphide is very slowly attacked.

446. Compounds of silver. Silver sulphide, Ag_2S, is a dark-gray-to-blue substance. It is practically nonvolatile at ordinary temperatures. Silver has a strong affinity for sulphur and readily combines with it. This sulphide is insoluble in alkalies and in their carbonates and chlorides. It is soluble in nitric acid and in potassium and sodium cyanides. Silver dissolves

readily in the molten sulphides of Cu, Fe, and Pb, and on this property is based the extraction of silver by smelting processes. Mercury decomposes the sulphide and forms an amalgam with the resulting silver. It is reduced by the sulphate in a manner similar to copper:

$$Ag_2S + Ag_2SO_4 = 4\,Ag + 2\,SO_2.$$

Silver chloride is another compound of silver which is important from a metallurgical point of view. It is produced in many metallurgical operations and is found native as cerargyrite. It is readily dissolved by hot solutions of sodium hyposulphite, calcium, and magnesium chlorides, alkaline cyanides, and hydrochloric acid. Zinc and iron decompose it in a solution as follows:

$$2\,AgCl + Zn = 2\,Ag + ZnCl_2.$$

It is completely reduced when fused with alkaline hydrates and carbonates:

$$4\,AgCl + 2\,Na_2CO_3 = 4\,Ag + 2\,CO_2 + O_2 + 4\,NaCl.$$

Silver sulphate is another compound produced in large quantities in the parting operations incident to the refining of bullion. It is soluble in hot concentrated acid, but the best solvent is dilute H_2SO_4. From such a solution the silver can be completely precipitated by Cu, Fe, Zn, Sn, or Pb, although Cu is always used as the precipitant.

447. Ores of silver. Silver occurs in nature in both the native and the combined form. Native silver is found in flakes, wire-like forms, and masses. The latter have been found containing as much as 1500 pounds of the precious metal. Often the purity of this native silver is high — from 900 to 980 fine. The most common minerals of silver are argentite (Ag_2S), cerargyrite ($AgCl$), and stephanite (Ag_5SbS_4). Many others have been found and identified, but they do not constitute important sources of the metal.

Sometimes an ore is valuable for its silver content alone. The rich ore of Cobalt, Ontario, sometimes contains as high as 7000 ounces of Ag per ton. More often, however, the silver is associated with gold, both metals being extracted. A very large proportion of the world's supply of this metal is extracted from

lead, copper, and zinc ores, as indicated in Table XLV. The most important of these are lead, copper, and iron sulphides, which almost always contain small amounts of both gold and silver.

TABLE XLV. PERCENTAGES BY WEIGHT OF SILVER FROM VARIOUS SOURCES IN THE UNITED STATES

	1910	1915	1920	1925
Placers	0.28	0.21	0.13	0.08
Siliceous ores	40.15	35.53	36.22	25.63
Copper ores	27.82	25.96	21.49	27.06
Lead ores	26.09	27.40	30.19	28.15
Zinc ores	1.31	1.57	2.23	0.27
Complex ores	4.35	9.33	9.74	18.81

While some silver ores are phenomenally rich, — from 2000 to 7000 ounces of Ag per ton, — the bulk of the world's silver has been produced from relatively low-grade ores. It has already been shown, in the chapter on gold, how the character of an ore and its relation to cheap transportation affect its value. The same, of course, applies to the ores of silver. Under ordinary conditions, in the United States it does not pay to treat a silver ore when it contains less than 6 ounces of Ag per ton. Under exceptional circumstances ores as low-grade as 3 ounces of Ag per ton are now being treated.

448. Production. As indicated in Table XLVI, the United States, Mexico, Canada, and Central and South America produce most of the world's silver. This production varies between wide limits, according to business conditions, the development of new mines, and the processes of extraction. For example, the discovery of the mines of Cobalt, Ontario, several years ago almost tripled the production of silver in Canada. As these mines were exhausted, production fell to about a third of its former value, and it is now at about one half of that value. China and India, through the national custom of hoarding, consume large amounts of silver, so that the production of this metal depends very greatly upon political and business conditions in these countries. For example, during 1923, although no silver was purchased by the government for coinage in India, that country imported over 100,000,000 ounces. During the same period China consumed 75,000,000 ounces.

TABLE XLVI. WORLD'S PRODUCTION OF SILVER (IN TROY OUNCES OF FINE SILVER)*

	1910	1915	1920	1925
United States	57,137,900	74,961,075	55,361,573	66,106,922
Canada	32,869,264	28,401,503	12,793,541	20,228,988
Mexico	71,372,194	39,570,151	66,662,253	92,885,465
Bolivia, Chile	6,490,163	3,870,065	2,200,000 1,800,000	4,346,532 3,553,862
Peru	9,566,118	9,419,950	9,196,282	19,917,439
Germany	5,597,026	†	†	3,858,000
Spain	4,152,430	4,565,396	3,191,387	3,303,863
British India	44,772	284,875	2,870,595	4,854,923
Australasia	21,545,828	4,295,755	7,613,568	11,114,648
Central America	2,026,885	2,920,496	2,700,000	2,700,935
All others	12,076,782	11,464,712	9,823,487	12,266,595
Total	222,879,362	179,753,978	174,212,686	245,138,172

† Not available.

449. Marketing and prices. Most of our silver is marketed in the form of bars of commercial silver (99.9 per cent Ag) weighing from 1000 to 1200 ounces. Table XLVII gives the price range of this metal over a period of years. Silver is quoted in cents per troy ounce. As indicated, silver has varied between wide limits during the past few years. This has been in response to demand alone, for the metal is widely produced, no one country or group of companies controlling the output.

TABLE XLVII. AVERAGE ANNUAL PRICE OF SILVER

YEAR	CENTS PER OUNCE	YEAR	CENTS PER OUNCE
1910	53.49	1923	64.87
1915	49.68	1924	66.78
1920	100.90	1925	69.07
1921	62.65	1926	62.11
1922	67.52	1927	56.37

EXTRACTION OF SILVER FROM ITS ORES

450. General. Silver may be extracted from its ores either by dry smelting or by leaching methods, so that we can divide these processes into the following classes:

1. *Direct smelting.* Many so-called dry silver ores are mixed with suitable lead or copper ores and smelted as such in blast

* Annual Reports, Director of the Mint.

or reverberatory furnaces. The silver is absorbed by the matte or metal, as the case may be, and can be recovered in the process of refining. Most of the impurities, such as As, Sb, Fe, Zn, etc., are eliminated as fume or are dissolved in the slag.

2. *Amalgamation processes.* *a.* The patio process has been in use in Mexico and South America for over three hundred years. The finely crushed ore is spread out on a water-tight floor of a patio, or yard paved with flagstones. Water is added until the consistency of the mass is about that of common brick clay. Common salt (about 6 per cent of the ore) is added and mules or horses driven through the mass for several hours so that it will be thoroughly mixed. Copper sulphate and mercury are then added, the former to reduce the silver compounds, the latter to form an amalgam with this reduced silver. With high-grade ores, containing let us say 60 ounces of Ag per ton, the extraction often reaches 80 per cent. This process is of historic interest only and has been replaced either by cyanidation or by one of the leaching processes.

b. Pan amalgamation, like the patio process, is solely of historic interest. In this process the ore is ground, wet, to pass a 40-mesh screen. It is then ground in an amalgamating pan with mercury, which not only serves to pulverize the ore finer but by agitation brings every particle of the mass in contact with the mercury. Sodium chloride and copper sulphate are added in order to decompose any silver sulphide and aid in the amalgamation. In order to accelerate these reactions the pans are usually steam-jacketed. After about five hours of grinding, the pulp is transferred to a settling tank, where a separation between the amalgam, the base-metal sulphides, and the gangue is effected. The amalgam is subjected to distillation, while the sulphides are sent to a smelter for reduction.

3. *Cyanidation.* This process differs only in minor details of strength of solution and time of treatment from the cyanide process used in the recovery of gold.

4. *Other hydrometallurgical processes.* *a.* In the Augustin process the silver as AgCl is dissolved in brine and then precipitated with metallic copper.

b. In the Patera process the silver as AgCl is dissolved in a solution of sodium thiosulphite and then precipitated with sodium sulphide.

c. In the Ziervogel process the ore or matte is first roasted. The silver sulphate thus formed is then dissolved in hot water and precipitated with metallic copper. The process, while suitable for certain high-silver copper mattes, has been given up in this country, for such products can now be more cheaply smelted in blast furnaces and the silver afterwards recovered in the usual refining process.

d. In the Russell process the leaching solution is a double hyposulphite of copper and sodium.

Many modifications of the processes described above have been devised for the treatment of certain special ores or products. While some of them possess undoubted merit, most of them have been replaced by cyaniding or direct smelting. Only those now commonly used in the United States will be described in this text.

THE CHLORIDIZING ROAST OF SILVER ORES

451. General. Often the silver occurs in ores as a sulphide, arsenide, or antimonide and may be associated with many base-metal minerals such as pyrite, galena, chalcopyrite, etc. Such refractory ores cannot be successfully treated by simple amalgamation. An oxidizing roast is sometimes sufficient, but more often a chloridizing roast is necessary to render the ore amenable to amalgamation. The chloridizing roast must often be used in connection with some of the leaching processes.

452. Operation. The ore to be chloridized is crushed and ground to pass a 10-mesh screen, the more refractory ones to pass a 40-mesh. The roasting is carried out in a small reverberatory furnace with common salt, the object being to convert the silver into chloride. The reactions involved are as follows:

$$3\,FeS + 11\,O = 2\,SO_2 + FeSO_4 + Fe_2O_3. \quad (1)$$

$$FeSO_4 + 2\,NaCl = Na_2SO_4 + FeCl_2. \quad (2)$$

$$4\,FeCl_2 + 6\,O = 2\,Fe_2O_3 + 4\,Cl_2. \quad (3)$$

$$Ag_2S + O_2 + Cl_2 = 2\,AgCl + SO_2. \quad (4)$$

In the first stage of the roasting the ore is heated just enough to drive off the first atom of S from the pyrite and prevent the ore from agglomerating. The air then oxidizes the FeS to a mixture of Fe_2O_3 and $FeSO_4$ according to (1). Any As or Sb is

volatilized and thus eliminated from the ore. Any copper sulphide which may be present will be converted into a sulphate. The temperature of the furnace is then raised to about 600° C., whereupon the ferrous sulphate reacts with the salt to form chlorine according to (2) and (3). The chlorine thus liberated reacts with the silver mineral to form AgCl according to (4). It should be noted that pyrite is essential to the success of the process. The ore should contain from 3 to 8 per cent of S as pyrite; if this is not present, pyrite must be added with the salt. On the other hand, if the ore contains more than about 8 per cent of S as pyrite, it should be rough-roasted before the salt is added; otherwise a considerable quantity of the base-metal chlorides will be formed. Great care must be observed in the roasting, for unless a considerable quantity of $FeSO_4$ is formed there will be little chlorine generated and an imperfect chlorination. The ore thus prepared can then be treated by pan amalgamation or by one of the leaching processes.

CYANIDING

453. General. Cyanidation has replaced most of the older processes for the extraction of silver from its ores, although there are some refractory ores which are not amenable to it. Finely disseminated silver is dissolved in cyanide solution, but the coarse metal is practically insoluble in any reasonable length of time. Stephanite and silver ores containing antimony are but slowly soluble, and with these the cyanide consumption is very high. While the general principles of cyaniding and the apparatus used are similar to those employed in the extraction of gold, there are important differences in the two processes.

454. Chemistry of the cyanide process. When finely divided silver is brought in contact with a solution of potassium or sodium cyanide, the silver is dissolved according to the following equations:

$$2\,Ag + 4\,NaCN + O + H_2O = 2\,NaAg(CN)_2 + 2\,NaOH.$$

$$AgCl + 2\,NaCN = NaAg(CN)_2 + NaCl.$$

$$Ag_2SO_4 + 4\,NaCN = 2\,NaAg(CN)_2 + Na_2SO_4.$$

$$Ag_2S + 4\,NaCN = 2\,NaAg(CN)_2 + Na_2S$$

(very slow and requires excess of cyanide).

The silver thus dissolved may be precipitated with either Zn or Al according to the following equations:

$$NaAg(CN)_2 + 2\,NaCN + Zn + 2\,H_2O = NaZn(CN)_4 + Ag + H_2 + 2\,NaOH.$$

$$2\,NaAg(CN)_2 + 4\,NaOH + 2\,Al = 4\,NaCN + 2\,Ag + Na_2Al_2O_4 + 4\,H.$$

One part of Zn precipitates 1.7 parts of Ag, while 1 part of Al will precipitate 4 parts of Ag. In general, there are the following important differences between the cyaniding of silver ores and the cyaniding of gold ores:

1. The ore must be very fine, and the time of contact between it and the solution must be much longer than for gold. Under the same conditions metallic silver dissolves about half as fast as gold, or in exact proportion to their atomic weights. In the slime process from forty-eight to ninety-six hours are necessary for solution, while in treating sands the pulp must be held in the tanks for from ten to twenty-five days.

2. The cyanide consumption is much higher than in the treatment of gold ores. Two conditions contribute to this: first, the time of contact being longer, many reactions which do not occur between cyanide and base metals in the cyaniding of gold ores go to completion in silver cyanidation; second, the silver being present in much larger quantities (from 10 to 25 ounces per ton as against from 0.1 to 1 ounce with gold ores), more cyanide is required for the actual dissolving of the silver. The consumption of cyanide will range from 1.6 to 5 pounds per ton of ore as compared with from 0.4 to 1 pound per ton of ore in the case of gold ores.

3. Thorough aëration or oxygenation of the charge is absolutely necessary to insure the complete solution of the silver minerals.

4. Stronger solutions must be used than for the treatment of gold ores. This, of course, brings about a higher consumption of cyanide.

5. On the whole, the cost of treatment is higher than for gold ores, since the time of treatment is longer and additional tanks and a more extensive plant are necessary. That, with increased cyanide consumption, accounts for a higher operating cost.

455. Precipitation of silver with aluminum. Aluminum dust has been used in place of zinc as a precipitant of silver from cyanide solutions. The following equation probably represents the reaction which occurs:

$$2\,NaAg(CN)_2 + 4\,NaOH + 2\,Al = 4\,NaCN + 2\,Ag + Na_2Al_2O_4 + 4\,H. \quad (1)$$

The mode of operation is similar to that employed in the precipitation by zinc dust, except that a longer time of contact is necessary and extra precautions must be taken to insure a complete emulsification of the Al dust, for it is not nearly so easily wetted by the solution as is zinc dust. The fact that Al does not replace the precious metals in cyanogen compounds makes necessary the presence of sodium hydroxide. One vital point should be noted: that at the time of precipitation lime must be absent from the solution, for lime reacts with the sodium aluminate according to the following equation:

$$Na_2Al_2O_4 + Ca(OH)_2 = CaAl_2O_4 + 2\,NaOH. \quad (2)$$

This calcium aluminate is insoluble and forms a deposit on the inside of the pipe lines, tanks, etc., which causes a great deal of trouble and annoyance.

This process has several advantages. From equation (1) we see that there is a regeneration of cyanide in the process, and the saving thus effected is considerable. In treating ores containing As and Sb it is found that zinc forms harmful compounds with these metals and causes a serious decrease in the dissolving power of the cyanide solution. This may be overcome to a certain extent by the use of Al as a precipitant. Another drawback is met with in the filtration of the pulp, for it is found that much of the calcium aluminate deposits in the fibers of the filter medium, reduces its porosity, and lengthens the filtration cycle. At a certain large plant, where tests were run with both Zn and Al, it was found that the costs per ton were zinc \$0.076, aluminum \$0.071, and soda ash \$0.036, showing that the aluminum process cost \$0.031 per ton more than the zinc but resulted in a saving of \$0.18 per ton in cyanide, giving a net saving of about \$0.15 per ton of ore. This is well worth considering when treating very low-grade ores.

CYANIDE PRACTICE

456. Ore. As in most fields of metallurgy, practice varies between wide limits according to the location of the plant, the physical and chemical character of the ore, the price of the metal, etc. The following data and flow sheet are given as representing practice at a modern plant.

The Rosario mill of the New York, Honduras, and Rosario Mining Company at San Juancito, Honduras, is a good example of a small but very efficient silver mill.* The tenor of the ore now being treated is indicated by the following composite sample, taken over a period of several months:

SiO_2	75.5 per cent
Al_2O_3	8.9 per cent
Fe	3.6 per cent
Mn	1.0 per cent
CaO	0.5 per cent
MgO	1.5 per cent
Pb	0.32 per cent
Zn	0.35 per cent
Sb	0.03 per cent
S	1.22 per cent
As and Bi	None
Ag	34.9 ounces per ton
Au	0.06 ounce per ton

Following, in Fig. 145, on page 354, is a flow sheet of the present mill.

457. Crushing. The ore is hauled from the mine by an electric locomotive in cars, each holding 1.15 dry tons and weighed on track scales. The ore is dumped, by means of a car tipple, onto stationary grizzlies with bars spaced 3 inches apart. The oversize from these grizzlies is sorted, suitable pieces of rock being removed to the tube-mill rock bin. The remainder of the oversize is crushed in two No. 4 Gates gyratory crushers.

There are four batteries of five 1850-pound gravity stamps. The stamping is done in cyanide solution with single-issue mortar boxes. The height of drop is 8 inches, with 108 drops per minute. The size of screen used varies, according to the tonnage desired, from 1 inch to 6 mesh (screen opening, 1.05 inch to 0.131 inch). Vanadium steel cam shafts 7 inches in diameter

* *Engineering and Mining Journal-Press*, July 18, 1925.

are used and have an average life of one year. When dies have been in service for about six weeks, they are removed from the mortar box and reshaped by means of a power-driven hack saw.

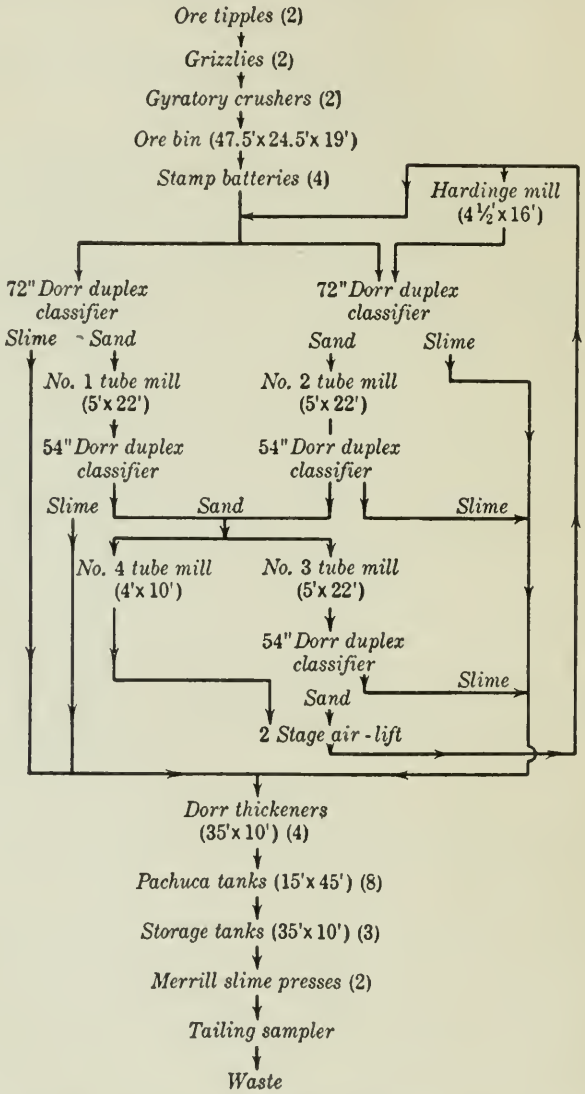

FIG. 145. Flow sheet of Rosario mill

Courtesy of the *Engineering and Mining Journal-Press*

Since the alloys are expensive and transportation costs high, this results in a considerable saving. The height of discharge is maintained fairly constant by the use of false bottoms under the dies and chuck blocks. The table on the opposite page gives sizing tests on the battery discharge for the different screens, the height of discharge being $3\frac{3}{4}$ inches.

Width of Screen in Inches	Ratio of Liquid to Solid	Mesh						
		+ 10	+ 40	+ 80	+ 100	+ 120	+ 150	− 150
1.05	13.7 : 1	51.03	27.59	9.65	1.38	1.38	1.38	7.59
0.742	16.0 : 1	45.00	26.70	11.65	1.68	1.66	1.66	11.65
0.525	11.3 : 1	44.44	30.86	10.48	1.85	1.85	1.23	9.29
0.371	10.0 : 1	31.93	33.13	15.06	3.66	2.41	3.00	10.81
0.263	9.6 : 1	28.17	38.77	12.25	4.08	2.45	2.45	11.83
0.185	7.6 : 1	15.00	42.00	19.50	3.50	4.00	2.50	13.50
0.131	8.3 : 1	4.24	49.10	21.21	4.24	4.28	4.20	12.73

458. Grinding. The battery discharge flows into a box, where the necessary milk of lime is added. From this box it is conducted by means of a launder to a 72-inch Dorr duplex classifier set at a slope of 13.6 per cent. The slime from each of these classifiers goes to the Dorr thickener, and the sand goes to a 25 × 5 foot Gates tube mill using as a grinding medium portions of the ore selected for this purpose from the grizzly oversize. This rock varies in size from 9 to 5 inches (average diameter, $6\frac{1}{2}$ inches) and is charged twice a day into the tube mill through the manhole. The tube-mill discharge (from Mills No. 1 and No. 2) is screened, the oversize going by a bucket elevator to the gravel bin, the undersize to two 54-inch Dorr duplex classifiers set at a slope of 15.1 per cent. The slimes from these classifiers go to the Dorr thickeners, the sands to one Gates tube mill (No. 3) and to one Chalmers-Williams ball tube mill (No. 4). The No. 3 tube mill is loaded with the same material as No. 2. If a large tonnage is expected, however, this mill is charged with 3-inch and 4-inch imported pebbles, which are more efficient on fine sand.

The Gates tube mills are lined with manganese-steel rib linings and last from one and one-half to two years, on Mills No. 1 and No. 2, and about a year longer on No. 3. When the first holes develop in the rib linings, they are patched by arc welding, which prolongs the life of the liners about six months. The Gates tube mills are each driven through a spur, pinion, and countershaft by a 75-horse-power motor.

The No. 3 tube-mill discharge flows to a 54-inch Dorr duplex classifier set at a slope of 11.4 per cent. The slime goes to the thickeners; the sand, to a two-stage air lift operated under 28 pounds pressure. The No. 4 tube-mill discharge goes without classification to the air lifts. The air lifts discharge into a

launder leading to the distributing box below the batteries. If at any time there should be an excessive circulating load, part of this air-lift discharge may be by-passed to a classifier which feeds a Hardinge ball mill. The accompanying table shows the work of the different mills:

Mesh	Sizing Tests					
	Tube Mills Nos. 1 and 2		Tube Mill No. 3		Hardinge Mill	
	Feed	*Discharge*	*Feed*	*Discharge*	*Feed*	*Discharge*
+ 30	50.5	3.1	5.8	0.2	0.5	0.0
+ 80	30.8	39.8	51.1	32.3	47.0	19.0
+ 100	6.7	11.3	13.1	14.1	20.5	12.0
+ 120	3.2	5.7	6.5	8.4	10.0	7.5
+ 150	2.9	5.6	5.8	8.5	9.5	14.0
+ 200	3.8	15.6	10.3	16.4	11.5	17.5
− 200	2.1	18.9	7.4	20.1	1.0	30.0

459. Thickening. Four single-tray Dorr thickeners, each 35 feet in diameter and 10 feet deep, receive as feed the overflow from the Dorr classifiers after it has passed a small cone. The purpose of the cone is to separate and throw back into the grinding circuit any coarse sand and concentrate that may have escaped over the lower end of the classifiers. The overflow of the thickeners is handled by three Aldrich triplex pumps, one 6 × 9 inches, the other two 10 × 10 inches.

Pneumatic agitation is used, and air for this purpose is provided by a 75-horse-power Ingersoll Rand compressor with free-air capacity of 1000 cubic feet per minute. The spigot from the Dorr thickeners enters a vat, where the cyanide is added, at about 39 per cent solids, and then passes to one of the eight Pachuca tanks, each 15 feet in diameter and 40 feet high. The individual charging system is used and is preferable in this case to the continuous system, owing to the fact that the ore at times shows wide variation in both composition and grade. For this reason a minimum amount of cyanide is added to each tank, although subsequent analysis may indicate the necessity of further addition to some particular charge. The tanks are agitated with air at a pressure of 28 pounds per square inch. Below the Pachuca tanks are three more mechanically agitated tanks, each 35 × 10 feet. The last agitator is used as a feed tank for the Merrill slime presses, and the three together

serve as surge tanks for the whole system. The total period of contact of the ore with the cyanide solution is about as follows:

From the battery to the thickener discharge	5 hours
In the agitators	74 hours
In the slime press	1½ hours

During the last two years both 96–98 per cent white sodium cyanide and 48 per cent black cyanide have been used. No lead acetate is necessary, because more than enough lead is extracted from the ore to precipitate the soluble sulphide derived from low-grade cyanide.

460. Filter-pressing. Filter-pressing is carried on in two Merrill slime presses, with a No. 6 duck as filter medium. On an average the press charge contains 10.25 tons of dry slime. A typical cycle is as follows:

Charging	12 minutes
Solution wash	55 minutes
Water wash	10 minutes
Air blow	6 minutes
Discharge	18 minutes

The air blow has been used during the last two years and has effected considerable savings in both soluble silver and cyanide. The cloths do not seem to be damaged by this air blow, and the presses sluice out much cleaner.

All leaks and drips from the press are caught and returned to the precipitation circuit. The filtrate from the Merrill presses goes to two storage tanks (20 × 10 feet), each of which is provided with a sand filter. One 6 × 9 inch and two 5 × 6 inch Aldrich triplex pumps elevate the discharge of these clarifying tanks a vertical height of 312 feet to the refinery, where it is stored in a 20 × 20 foot refinery head tank. The press canvas lasts for about 1200 charges and is acid-treated twice during this time.

461. Precipitation. The Crowe vacuum process and the Merrill precipitation equipment are used. It has been found that about 1 pound avoirdupois of Merrillite will precipitate 22 troy ounces of fine bullion. A vacuum of 90 per cent has been maintained over considerable periods of time. The zinc dust is fed to the intake of one 6 × 9 inch and two 5 × 6 inch Aldrich triplex pumps, which send it on to the precipitation presses.

There are four 36-inch Merrill precipitation presses. The average grade of precipitate is 85 per cent, although there is considerable fluctuation when increasing amounts of lead and copper are found in the ore. The precipitate is dried in electrically heated tray driers and melted in two oil-fired Case tilting furnaces using No. 275 graphite crucibles, from which from three to four 115-pound bars of bullion are obtained. The bars are dressed, weighed to the nearest tenth of an ounce, assayed, and shipped to the United States.

A close control of all operations is maintained by means of frequent samples. A moisture sample is taken at the ore scale, one shovelful from the first and one from the last car of every train. Pulp and drip samples are taken in the usual way throughout the mill. The following table indicates the average assay value of some of these mill samples for the year 1924:

	Ag	Au	Total KCN	Free KCN	CaO
	Ounces per Ton	*Ounces per Ton*	*Per Cent*	*Per Cent*	*Per Cent*
Mill heads	31.855	0.0618	—	—	—
Tank heads	19.847	0.0150	—	—	—
Press pulp heads	3.059	0.0034	—	—	—
Press pulp tails	2.712	0.0029	—	—	—
Mill solution	2.497	0.0210	0.453	0.240	0.061
Rich solution	13.013	0.0282	—	—	—
Refinery heads	4.973	0.0106	0.489	0.264	0.030
Refinery tails	0.058	0.0002	—	—	—
Press final solution	0.193	0.0005	0.351	—	—
Press discharge solution	0.042	0.0001	0.023	0.013	—

462. Supplies and costs. The following tables also indicate the cost per ton milled, consumption of supplies, and screen analysis of a mill tailing:

Screen Analysis of Mill Tailing

Mesh	Per Cent by Weight of Total Product	Assay Value in Ounces of Ag	Per Cent of Total Value
+ 80	1.60	2.05	1.15
+ 100	3.35	1.75	2.01
+ 120	2.84	1.87	1.87
+ 150	4.94	1.95	3.38
+ 200	15.21	2.24	11.93
− 200	72.06	3.16	79.66

CONSUMPTION OF SUPPLIES PER TON OF ORE MILLED

Tonnage = 75,710. Grade of ore = 31.9 ounces of silver per ton

96–98 per cent sodium cyanide	1.944 pounds
48 per cent cyanide	8.087 pounds
Zinc dust	1.371 pounds
Muriatic acid	0.076 pound
Lime (44.8 per cent)	36.313 pounds
Imported pebbles	1.514 pounds
Tube-mill rock	95.232 pounds
Borax glass	0.097 pound
Soda	0.050 pound
Refinery fuel oil	0.091 gallon

COSTS PER TON MILLED, 1923

Silver currency: 2 pesos, Honduras = 1 United States dollar

	LABOR	POWER	SUPPLIES
	Pesos	*Pesos*	*Pesos*
Superintendence	0.09774	—	0.00009
Sampling	.00727	—	.00001
Assaying	.04511	—	.04774
Lighting	—	0.00211	.00947
Repairs to buildings	.00658	—	.00505
Repairs to slime canal	.02846	—	.00973
Crushing	.07989	.00516	.01105
Stamping	.13047	.04648	.14723
Grinding	.14453	.09296	.35787
Pumping mill solution	.03474	.02582	.03246
Lime treatment	.02537	—	.59970
Cyanide treatment	.07811	—	1.95550
Agitation and thickening	.12670	.05682	.09477
Operating Merrill press	.07580	—	.22886
Pumping filter solution	.03259	.01806	.00583
Precipitation	.03965	.01292	.32729
Collecting and drying precipitate	.02176	—	.00312
Fluxing and melting	.05132	—	.18824
Slag treatment	.01989	—	.00080
Total	1.04598	.26033	4.02481

Mill costs per ton milled = $2.67, United States currency. Mill costs per fine ounce produced = 11.5 cents. Tonnage = 87,900 dry tons.

TINTIC STANDARD PLANT

463. Ore. The Augustin process is not in use in the United States today, but the modification of it which is described in the following sections is proving very successful at the plant of the Tintic Standard Mining Company at Harold, Utah. This

plant has a capacity of 200 tons per day and is operating on an ore of the following composition. For successful operation it is essential that the lime content be low, that the sulphur be not over 4 per cent, and that the gold be negligible.

Cu	0.3 per cent
Pb	5.0 per cent
SiO_2	65.0 per cent
Fe	10.0 per cent
CaO	0.7 per cent
S	3.0 per cent
As	0.7 per cent
Ag	18.26 ounces per ton
Au	0.025 ounce per ton

The flow sheet of the plant is shown in Fig. 146. The run-of-mine ore is crushed in a gyratory set at 3 inches and a Symons disk crusher set at $\frac{3}{4}$ inch. These machines are also used to crush the crude salt and coal required for the process. At the top of the mill there are seven 90-ton bins. Five of these are for ore, one for salt, and one for coal. The fine grinding equipment consists of two sets of 16 × 48 inch Allis-Chalmers rolls and three Mitchell vibrating screens. They operate in closed circuit so that all the material must pass a screen with an opening measuring 0.071 inch.

464. Roasting. Ore and salt, in the proportion of 10 to 1, are mixed before entering the mills, a composite sample being taken for each run of 75 tons. This goes to a separate "fine" bin and constitutes a mill lot. Every lot is analyzed for metals and sulphur, the latter being especially important, as it regulates the quantity of coal that must be used. The ideal condition is to have 3 per cent of sulphur (that is, sulphide sulphur not absolute sulphur) in the ore, to which 30 pounds of coal per ton of charge is added, bringing the total fuel to the equivalent of 5.3 per cent of sulphur. It would be easy to get 5.3 per cent of sulphur in the ore, but that will not do, because excessive sulphides produce a more fusible charge, with disastrous results. Sometimes two mill-lot bins may be drawn upon and mixed to get a better-proportioned charge. Ordinarily, however, a 3000-pound charge is drawn from one bin into an electrically operated charge car, the body of which is swung on a set of scales. This charge car empties into a concrete mixer to which the

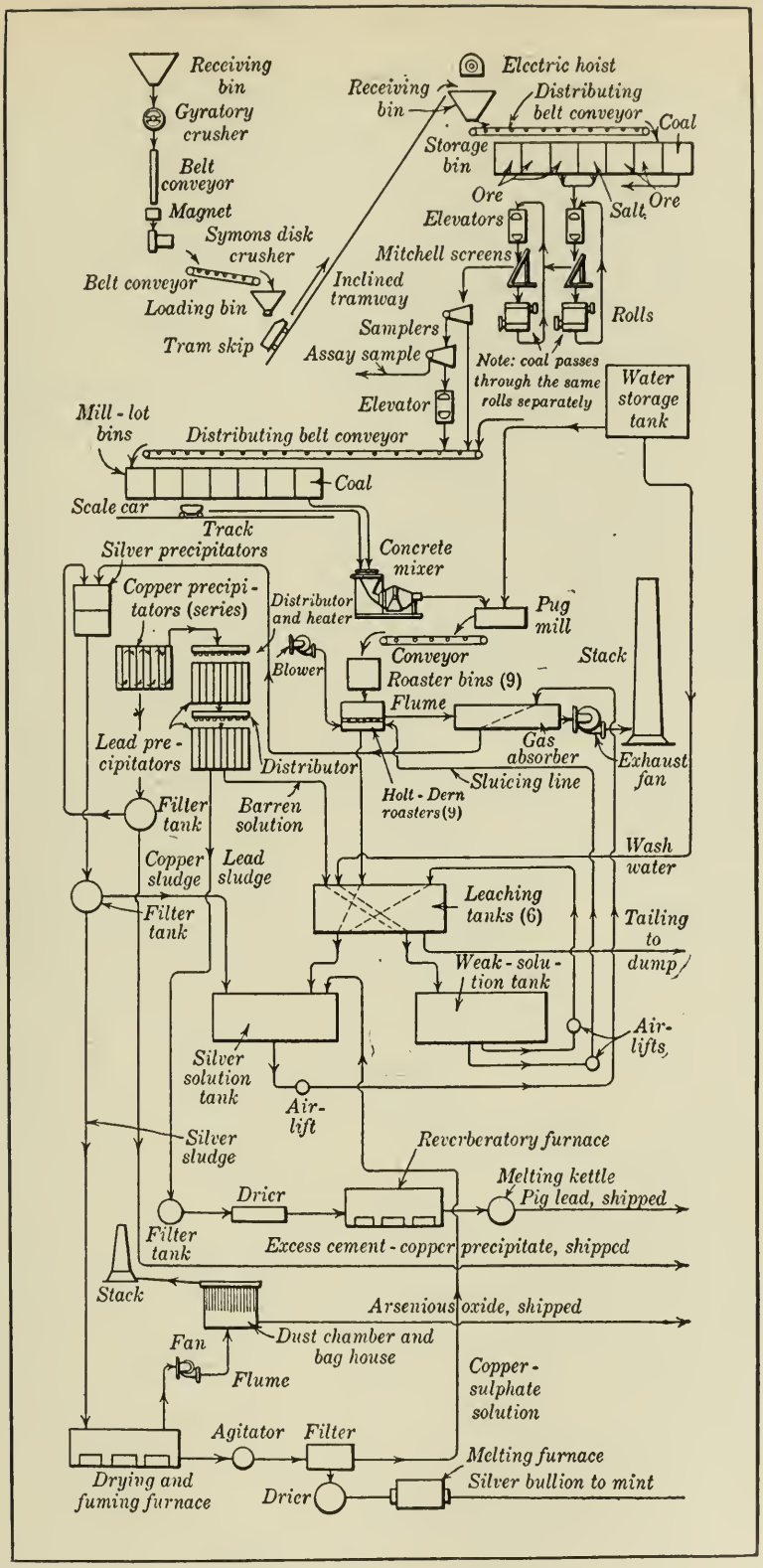

FIG. 146. Flow sheet of the Tintic Standard plant

Courtesy of the *Engineering and Mining Journal-Press*

weighed coal is also fed. After thorough mixing, the charge passes through the pug mill, where the necessary water (from 6 to 7 per cent, depending on the fineness of the ore) is added and further mixing is accomplished. It has been found that the best condition is to have the ore, salt, and coal mixture just damp enough to adhere, like molder's sand.

A system of belt conveyors delivers the mixture to the bins above the Holt-Dern roasters, of which there are nine, set end to end. The furnace is shown in section in Fig. 147. It consists of a reënforced-concrete box, 7 by 9 feet and 5 feet deep inside. On the bottom are mechanically operated grates provided with hoppers underneath. Leading into these hoppers is a pipe through which air under a pressure of 8 ounces per square inch is supplied to cool the roasted ore and heat the blast. A common flue, through which the waste gases are withdrawn, runs the length of the furnace. This connects with the absorption chamber, where the acid is recovered.

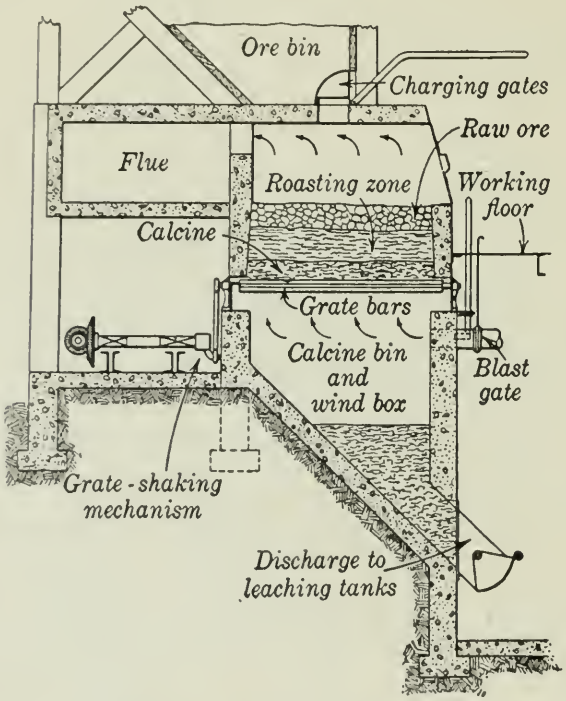

FIG. 147. Holt-Dern roaster

The furnace is started with a layer of coal dust dampened with oil, spread over the grate, and ignited. A special ore mixture, rich in coal, is added, the blast is turned on, and when the furnace is operating properly the routine charge is added. At regular intervals the grate mechanism is set in motion, and the charge is lowered in the furnace until a 10-inch bed of red-hot calcine is left on the grate ready for the new charge. This is added on top in 4-ton lots. The capacity of each furnace is about 25 tons of calcines per day. The temperature of the center of the roasting ore is between 700° and 750° C. The top is kept cool to avoid loss through volatilization. The chemical

reactions taking place ultimately may be represented by the following equations:

$$\mathrm{Ag + Cl = AgCl},$$
$$\mathrm{4\,Ag + O_2 + 4\,HCl = 4\,AgCl + 2\,H_2O},$$
$$\mathrm{4\,Ag + O_2 + 4\,NaCl = 4\,AgCl + 2\,Na_2O},$$
$$\mathrm{PbCO_3 + 2\,NaCl = PbCl_2 + Na_2CO_3},$$
$$\mathrm{CuSO_4 + 2\,NaCl = CuCl_2 + Na_2SO_4}.$$

The presence of pyrite is essential to the complete chlorination of the silver, probably as follows:

$$\mathrm{FeS_2 + 3\,O_2 = FeSO_4 + SO_2},$$
$$\mathrm{FeSO_4 + 2\,NaCl = FeCl_2 + Na_2SO_4},$$
$$\mathrm{4\,Ag + 2\,FeCl_2 + 3\,O = 4\,AgCl + Fe_2O_3}.$$

It is needless to say that the crux of the entire process is the roast, for if a satisfactory percentage of each valuable metal is chloridized, the leaching and precipitation are easily effected and a good recovery is obtained.

465. Leaching. While still hot the calcine is sluiced with a strong brine solution to one of the leaching vats. This solution, in plant parlance, is designated as weak because it is low in silver content. Sluicing has several advantages over dry handling, of which the freedom from dust and the utilization of the heat in the calcine for raising the temperature of the mill solution are most important.

The leaching vats, six in number, are 28 feet in diameter by 11 feet deep, each holding about 225 tons of calcine. The leaching bottom is made up of clean quartz sand in a skeleton work of wood. These tanks provide a clear filtrate and have given good service for more than a year. The vats are emptied of tailing by sluicing through the discharge gates with water. The usual cycle is about as follows:

Filling	24 hours
Weak-solution leach	48 hours
Barren-solution leach	48 hours
Washing	8 hours
Draining	4 hours
Sluicing	8 hours

Barren solution is obviously that from which the silver, copper, and lead have been precipitated. When a barren solution has passed once through a leaching vat, it becomes a weak solution,

and when a weak solution has passed through a vat, it becomes a silver solution. About 7 tons of solution per ton of roast are used in leaching.

466. Precipitation. The silver, or "pregnant," solution, containing about 5 ounces of silver per ton, is conditioned for precipitation by being sprayed into an acid-absorbing chamber. This is simply a 40-foot section of the roaster-gas flue, where some hydrochloric acid and sulphuric acid are absorbed, but in addition it has been found necessary to add some commercial sulphuric acid. The total acidity as expressed by H_2SO_4 is maintained at between 2 and 5 pounds per ton of ore. Air lifts with columns of wood are used for pumping the hot corrosive liquors.

The precipitation of silver with the copper is accomplished in a set of four concrete agitators each 10 feet square and 18 feet deep, with hopper bottoms. Air lifts similar to those in a Pachuca tank maintain the agitation, and a baffle, or partition, along one side of each provides a quiet settling column, so that fairly clear overflow may pass from each agitator to the next, or, in the case of the last, to the copper-precipitating vats. The present practice is to operate two units consisting of two agitators in series. When precipitation is completed in one unit, the entire flow is diverted to the other. The excess liquor is siphoned off and the precipitate is sluiced to the filter press. A typical analysis of crude silver precipitate is as follows:

Gold	0.005 ounce per ton
Silver	8000 ounces per ton
Copper	15.0 per cent
Lead	1.0 per cent
Arsenic	15.8 per cent

This precipitate is given a threefold treatment in a small reverberatory furnace, involving (1) drying, (2) distillation of the arsenic, and (3) oxidation of copper by roasting. The copper is then leached out with sulphuric acid, leaving, after washing and filtering, a precipitate of the following analysis:

Gold	0.005 ounce per ton
Silver	15,400 ounces per ton
Copper	1.1 per cent
Lead	1.8 per cent
Arsenic	0.7 per cent

This precipitate is dried, melted, and cast into bullion for shipment to the mint, where it is refined.

The effluent from the silver-precipitators is now ready to pass through the "iron boxes" for the precipitation of copper and the remaining silver. These consist of eight large reënforced-concrete launders measuring 8 by 32 feet with 2 feet of average effective depth. The bottoms slope, to facilitate sluicing, and are provided with wooden covers to conserve the heat. Either heavy scrap iron or tin-plate cuttings are used for precipitating lead — preferably the latter.

The solution passes through the eight boxes in series, one box being by-passed and washed each day. The sludge is sluiced to a filter press. The following table indicates a typical analysis of this product:

Gold	0.005 ounce per ton
Silver	134 ounces per ton
Lead	6.0 per cent
Copper	63.5 per cent
Sulphur	0.6 per cent
Insoluble	3.5 per cent
Iron	3.4 per cent

The effluent from the iron boxes, which, under ideal conditions, is maintained at about 45° C., is now raised to 85° C., preparatory to precipitation on the de-tinned scrap. This heating is done by means of copper coils, through which steam circulates. The feed solution contains 15 pounds of lead per ton, and about 90 per cent of this is precipitated under ordinary conditions. The precipitant is scrap tin plate from which the tin has been removed in a small auxiliary plant. The following analysis indicates the composition of the average precipitate:

Gold	0.005 ounce per ton
Silver	3.4 ounces per ton
Lead	69.25 per cent
Copper	5.9 per cent
Sulphur	0.5 per cent
Insoluble	1.0 per cent
Iron	5.9 per cent
Alumina	4.5 per cent

It is quite essential that operations be closely controlled, or the entire process is likely to be disrupted and recovery spoiled. If the tonnage treated, the sulphur content of the ore, the

temperature, and the specific gravities of the various solutions are kept fairly constant, everything works well. If the ore contains more than 4 per cent of S, sintering is sure to occur in the roasters. If the furnaces do not shake down properly, the chloridizing is unsatisfactory and the roasting capacity is greatly reduced. Low tonnage, on the other hand, causes the temperature and specific gravities of the circulating solutions to fall, and, owing to the low temperature, lead chloride tends to precipitate in the pumps, launders, and other inconvenient places. When the specific gravities fall, the chlorine content of the leach solutions diminishes and the extraction of both silver and lead suffers. Experience has shown that the best temperatures are as follows:

Silver-precipitators	40° C.
Copper-precipitators	45° C.
Lead-precipitators	85° C.

The recovery for 1924 averaged as follows:

Silver	87.6 per cent
Copper	59.8 per cent
Lead	32.4 per cent
Gold	7 per cent

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CHAPTER XII

ALUMINUM AND MAGNESIUM

ALUMINUM

467. General. Although aluminum is one of the most abundant metals in the earth's crust, it was considered a rare one as recently as the middle of the nineteenth century. Today, such has been the progress in methods of reduction and refining, it has established for itself a very important place among the nonferrous metals. Low specific gravity, malleability, high thermal and electrical conductivity, ductility, and resistance to corrosion make this metal a very valuable engineering material.

In 1890 aluminum sold for $2.38 per pound, and only 110 tons per year were produced in the whole world. Today the world's production is in the neighborhood of 325,000 tons per year, and the metal sells for about $0.22 per pound.

468. Physical and chemical properties. Aluminum is a bluish-white metal, lustrous, highly malleable, and ductile. It has a specific gravity of 2.70 at 20° C., melts at 658.7° C., and boils at 1800° C. It is relatively soft — Brinell hardness, 25. The tensile strength of the pure cast metal is 18,000 pounds per square inch; that of the rolled sheet and drawn wire, as high as 40,000 pounds. Aluminum remains practically unchanged in air or water, owing to the formation of a thin coat of the oxide. It is acted upon by the strong acids and bases. It alloys readily with copper, tin, nickel, zinc, and tungsten.

469. Ores. While aluminum is the most abundant of the common metals, constituting about 7 per cent of the earth's crust, the compounds or ores from which it can be obtained are relatively few. Aluminum is a constituent of most of our common rocks, such as granite, syenite, shale, clays, micas, etc. It is commonly obtained in pure form from only two minerals — bauxite and cryolite.

Bauxite ($Al_2O_3 \cdot H_2O$ to $Al_2O_3 \cdot 3\,H_2O$) is an earthy mineral, light cream to deep red in color, depending upon the iron content. It occurs mixed with many impurities, such as silica, iron oxide, titanium, and copper. Although it is found in many places in the world, the deposits of economic importance are but few. In the United States, Arkansas, Alabama, and Georgia formerly yielded the bulk of our supply, but at present British Guiana furnishes a very large tonnage. In the Old World, France, Austria, and Germany produce the most. Commercial bauxite ranges in composition between the following extremes:

	Per Cent
Al_2O_3	45–70
SiO_2	2–30
Fe_2O_3	3–25
H_2O	12–40

Cryolite ($3\,NaF \cdot AlF_3$) is found in commercial quantities in only one place in the world — at Ivigtut in South Greenland. In the beginning of the industry it was the chief source of aluminum in the United States. While not an important source of aluminum at present, it is an essential constituent of the igneous bath used in the electrolytic reduction of the metal. The largest domestic company now prepares its cryolite synthetically.

470. Uses. Aluminum, in the form of sheets, rods, bars, and castings, is used as a structural material where lightness is essential. The manufacture of cooking utensils, motor cars, aircraft, wire, and cable consumes large amounts of this metal. In the manufacture of chemicals and paints, in the deoxidation of steel, in thermite welding, and in the making of explosives this metal is equally important. As a matter of fact, new uses are being found for this interesting metal every day. As compared with iron and steel relatively little research has been made on the aluminum alloys and their heat treatment, so that this is almost a virgin field for the metallurgist.

471. Production. Since the development of the Hall process the production of aluminum has increased more rapidly than that of any other metal. Today, in point of tonnage, it is exceeded only by iron, copper, lead, and zinc. It is not at all unlikely that the next decade will witness new developments

in the metallurgy of this wonderful metal, and will find it in more common use than either lead or zinc. The world's production of primary aluminum is given in Table XLVIII.

TABLE XLVIII. WORLD'S PRODUCTION OF ALUMINUM (IN METRIC TONS) *

YEAR	CANADA	FRANCE	GERMANY	GREAT BRITAIN	NORWAY	SWITZERLAND	UNITED STATES	ALL OTHERS	TOTAL
1910	3,858	10,472	—	5,512	992	—	6,000	—	26,834
1915	8,490	6,020	2,000	6,000	3,500	12,500	45,000	3,400	86,910
1920	10,000	12,304	10,000	8,000	5,000	12,000	90,000	3,238	150,542
1921	6,000	8,380	10,000	5,000	4,000	10,000	28,750	2,744	74,874
1922	9,000	7,494	12,000	9,500	6,000	12,000	52,000	4,810	112,804
1923	16,500	14,343	15,900	9,000	13,320	12,000	95,000	5,472	181,535
1924	16,000	18,500	18,400	7,000	19,900	19,000	85,000	4,206	188,006
1925	17,000	20,500	25,000	9,000	23,000	20,000	93,000	5,830	213,330
1926	18,000	21,000	30,000	7,000	22,000	20,000	91,000	4,500	213,500

472. Marketing and prices. There is but little competition in the sale of domestic primary aluminum. There is only one producing company in this country, and that one, aided by a substantial tariff, virtually controls the domestic market. There is rarely enough of the metal to meet market needs. Whether this is due to increasing demand or to market manipulation is a debated question. Probably the former, because this domestic company is now erecting a very large plant in Canada.

Primary aluminum is sold in the form of ingots, powder, sheets, and various structural forms. The ingots are usually in the form of notched bars weighing 3 pounds, but for special orders they are made in sizes up to 30 pounds. The price range of the pure metal during recent years is given in Table XLIX.

TABLE XLIX. PRICES OF ALUMINUM IN NEW YORK

YEAR	CENTS PER POUND
1910	22.10
1915	33.98
1920	30.62
1921	26.35
1922	20.05
1923	25.73
1924	28.30
1925	28.00
1926	27.00
1927	25.75

* Estimated.

Hall-Héroult Process

There are two distinct steps in the production of aluminum by this process: (1) the production of pure Al_2O_3 from the ore; (2) the reduction of this Al_2O_3 to metallic aluminum in the electric furnace.

473. Preparation of the pure alumina. It has just been stated that commercial bauxite contains relatively large amounts of impurities. Many of these, if allowed to contaminate the metallic aluminum, would seriously affect its physical or chemical properties. They must therefore be removed from the ore, for no practical methods have been evolved for preventing their reduction along with the aluminum. This preparation of pure Al_2O_3 constitutes one of the larger costs of the whole process, and although many other methods have been suggested, the Bayer process (in modified form) is still the one most commonly used in this country.

In the Bayer process the crude bauxite is ground to pass a 100-mesh screen and is then treated with an aqueous solution of NaOH in autoclaves at a temperature of 155° C. and at a pressure of from 50 to 70 pounds per square inch. After from two to eight hours of this treatment, sodium aluminate forms as follows:

$$Al_2O_3 + 2\,NaOH = Al_2O_3 \cdot Na_2O + H_2O.$$

Most of the impurities are unaffected, settle to the bottom of the container, and are discarded. Upward of 90 per cent of the aluminum is dissolved. The solution is diluted, passed through filter presses in order to remove the last trace of suspended matter, and then sent to the precipitation tanks. To this solution is added a small amount of freshly precipitated $Al_2(OH)_3$ and the whole is stirred while precipitation goes on thus:

$$3(Al_2O_3 \cdot Na_2O) + Al_2O_3 \cdot 3\,H_2O = 3(Al_2O_3 \cdot 3\,H_2O) + Al_2O_3 \cdot 3\,Na_2O.$$

$$Al_2O_3 \cdot 3\,Na_2O + 2\,Al_2O_3 = 3\,Al_2O_3 \cdot Na_2O.$$

At the end of about three days, when the precipitation is complete, the contents are drawn off and passed through filter presses. The cake from these is washed, dried, and calcined in rotary kilns, yielding a product containing from 98 to 99.5 per cent of Al_2O_3. This alumina is then ready for reduction.

474. Reduction of alumina. Nearly all the primary aluminum now made in this country is produced by a modification of the original Hall-Héroult process. This process depends upon the fact that alumina can be dissolved in a fused bath of aluminum fluoride. The application of an electric current to this bath results in the dissociation of the alumina as follows:

$$Al_2O_3 = 2\,Al + 3\,O.$$

The aluminum is liberated at the cathode and collects in the bottom of the cell, while the oxygen attacks the carbon anode and escapes as CO or CO_2.

The common type of electrolytic cell is shown in Fig. 148. It consists of a rectangular steel tank 8 feet long, 5 feet wide, and 2 feet deep. There is a refractory lining next to the steel shell and an inner lining of petroleum coke. The latter is connected with the source of current and serves as the cathode. The bottom is inclined toward the tap hole. The anodes are made of high-grade petroleum coke, from 3 to 16 inches in diameter and from 10 to 42 inches in length. They are suspended from the framework of the tank — from eight to twelve to each cell.

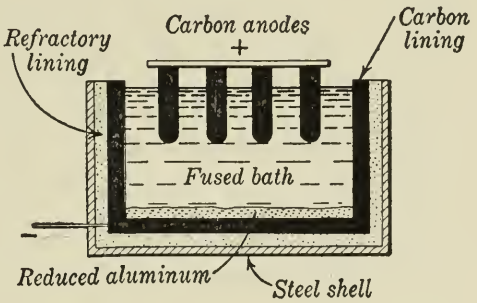

FIG. 148. Cell for electrolysis of aluminum

The theoretical voltage necessary to bring about the decomposition of the alumina is 2.8 volts, but it is found best to use about 7 volts in order to compensate for cell and resistance losses. The current density varies from 650 to 750 amperes per square foot. The composition of the bath is very important, since the separation of the aluminum, as well as the current efficiency of the process, depends upon it. The specific gravity of the bath must be less than that of the molten aluminum; otherwise it would rise to the top and be oxidized. A typical bath contains 59 per cent of AlF_3, 21 per cent of NaF, and 20 per cent of CaF. Such a bath at a temperature of 900° C. will dissolve about 20 per cent of Al_2O_3 and will have a specific gravity of 2.1 as compared with 2.31 of aluminum in the liquid state at that temperature.

475. Commercial aluminum. The impurities in the reduced aluminum are Cu, Si, Fe, and Al_2O_3. The grading of the metal depends upon the aluminum content (by difference):

Special	99.5 per cent Al or higher
Grade No. 1 or A	From 99.0 to 99.4 per cent Al
Grade No. 2 or B	From 98.0 to 99.0 per cent Al

All the metal from the reduction cell is ordinarily remelted before it is cast into pigs ($1\frac{3}{4} \times 1\frac{3}{4} \times 36$ inches). These have ten notches along the top in order that small pieces may readily be broken off for alloying. Until recently attempts to refine impure aluminum to produce a very pure metal (such as the electrolytic refining of blister copper) have not been very successful. The Hoopes process, which utilizes a three-layer bath, accomplishes this, and we are now able to produce commercially a metal with as high as 99.98 per cent of Al.

476. Aluminum alloys. The common alloys of aluminum are those with Zn, Cu, Mn, Si, Mg, and Fe. Up to a few years ago relatively few of these alloys were in common use, but research in casting and heat treatment have led to their widespread adoption. Indeed, it is safe to say that these researches have only scratched the surface of this fertile field. Hardly a tenth as much research has been devoted to aluminum as to iron and steel, and yet this light metal is already competing actively with lead and zinc as an engineering material.

An alloy containing 92 per cent of Al and 8 per cent of Cu (No. 12 alloy) is extensively used in making sand castings. Another popular alloy for this work is one containing 90 per cent of Al, 7 per cent of Cu, 1 per cent of Fe, and 2 per cent of Zn. Magnalium, a complex magnesium-bearing aluminum alloy, and silumin, containing from 5 to 15 per cent of Si, have also been used for this purpose. The number of such alloys is very large, but only the first two may be considered as standard.

Aluminum is malleable and ductile, and many of its alloys can be worked. The one in most common use is duralumin, the average composition of which is as follows:

	Per Cent
Cu	3.5–4.5
Mg	0.5–1.0
Mn	0.5–1.0
Al (by difference)	95.5–93.5

Forgings and structural shapes made from this alloy are extensively used in the automotive and aircraft industry. By quenching from about 500° C. and subsequent drawing, it may be materially hardened. The tensile strength when heat-treated may be as much as 55,000 pounds per square inch — approximately that of mild steel. Zinc duralumin of the following composition is made, having a tensile strength as high as 75,000 pounds per square inch:

	Per Cent
Cu	2.5
Mg	0.5
Mn	0.5
Zn	20.0
Al (by difference)	76.5

Another alloy of this type containing Ni and another containing Si have had some use.

477. Aging. In many aluminum alloys the tensile strength, Brinell hardness, and machining properties increase for some time after the alloy is cast. This phenomenon is called aging. This increase may in some instances amount to as much as 25 per cent in one month. Very often this change may be brought about more rapidly by drawing at a temperature of from 100 to 200° C.

MAGNESIUM

478. General. Even after the production of aluminum had been established at a moderate price, it required several years of extensive advertising by one of our large metallurgical companies to bring the American people to realize the value of this light metal. A similar situation now exists with its sister metal magnesium. Magnesium is now in common use in Europe and is actively competing with aluminum in Germany, but in this country the production at the present time is very little more than in 1915, when it first came to be used. It is safe to say that time and research will bring about a much wider use.

479. Physical and chemical properties. Magnesium is a silvery white metal resembling aluminum. It is the lightest metal used for engineering purposes, having a specific gravity of from 1.75 to 1.90. It melts at 651° C. and boils at 1120° C. It is relatively soft, with a Brinell hardness of 30 in the cast state. It has a

tensile strength, when cast, of about 13,000 pounds per square inch. Magnesium reduces most oxides. It is dissolved by dilute acids but resists caustic alkali solution. At ordinary temperatures water does not attack the metal, but at 100° C. it is slowly attacked, with the evolution of hydrogen. In dry air the metal does not oxidize, but in moist air it becomes coated with a mixture of the oxide, carbonate, and hydrate. The powdered metal burns rapidly in the air, emitting an intense white light of great value in photographic work.

480. Ores. The compounds of magnesium, like those of aluminum, are very common, occurring in most igneous and metamorphic rocks. Magnesium constitutes over 2 per cent of the earth's crust. The only compounds from which the metal has so far been obtained, on a commercial scale, are the oxide and chloride. These are commonly found in nature in a fairly high state of purity — the former as magnesite or dolomite, the latter in certain mineral or saline springs.

481. Uses. The largest use of metallic magnesium is for the deoxidation of other metals. Its affinity for oxygen and nitrogen is greater than that of any other common metal. Of the magnesium alloys, those with zinc, aluminum, cadmium, and copper are the most important. Aluminum-magnesium alloys find wide use in the manufacture of pistons, connecting rods, general reciprocating parts, aircraft parts, and scientific instruments. They constitute the lightest alloys used in engineering construction, being lighter than aluminum and yet possessing a tensile strength as high as 50,000 pounds per square inch. There is no doubt, as has been said before, that as metallurgists develop cheaper methods of reduction and the public becomes educated to appreciate its value, the consumption of this metal will increase very rapidly.

482. Production, marketing, and prices. The metal is marketed in a number of forms and grades, depending upon the use to which it is to be put. Like its sister metal aluminum, it is graded according to its magnesium content (by difference) as follows:

	Per Cent of Magnesium
No. 0	99.99
No. 1	99.85
No. 2	99.00

For fabrication and casting No. 0 or No. 1 is always specified, but for deoxidizing purposes No. 2 is sufficiently pure. Structural material comes in the form of sheets, plates, rods, wire, tubing, and castings. For deoxidizing and alloying it is marketed in the form of 8-pound ingots ($3 \times 3 \times 16$ inches) or 10-ounce sticks (1×12 inches).

The annual consumption in the United States is still very small, probably not over 250,000 pounds. This small consumption and the metallurgical difficulties of reduction have contributed to make the metal rather expensive. Pure ingots in 1927 sold at $1 per pound in 1000-pound lots. Other forms command higher prices, depending upon the difficulty of forming.

483. Reduction of magnesium. Of the many processes which have been suggested for the reduction of magnesium, only two are in common use. Both are electrolytic methods similar to the one used in the reduction of aluminum, one using magnesium chloride and the other magnesium oxide as the source of the metal. Reduction by sodium, by carbon, and by the electrolysis of aqueous solutions have all been tried and abandoned as impractical.

Magnesium Chloride Process

This process involves two distinct steps: (1) the preparation of anhydrous magnesium chloride; (2) the electrolysis of a fused bath.

484. Preparation of magnesium chloride. The preparation of anhydrous magnesium chloride is a difficult and expensive operation. Calcination of the common salt $MgCl_2 \cdot 6\,H_2O$ yields MgO (not $MgCl_2$), as indicated below:

$$MgCl_2 \cdot 6\,H_2O = MgO + 2\,HCl + 5\,H_2O.$$

Several other methods of preparation have been suggested. Perhaps the most successful consists in driving off a part of the water by heating at 150° C. When the reaction at this temperature is complete, the material is heated to 300° C. in a current of HCl gas, and the remaining water removed; this yields a product containing upward of 99 per cent of $MgCl_2$. The HCl may be recovered as a by-product for sale or returned to the process.

485. Electrolysis. A bath of anhydrous magnesium chloride or a mixture of this with NaCl or KCl is electrolyzed at about 700° C. in a cell, as shown in Fig. 149. Either the batch or continuous process may be used. The cell consists of a rectangular steel tank with carbon anodes and iron cathodes. The metal forms on the surface of the cathode, rises to the top of the bath and is removed by means of a ladle, and is cast into ingots or re-purified. To prevent the re-formation of $MgCl_2$ a porcelain hood catches most of the anodic chlorine. Any chlorine which may leak into the cathode compartment is swept away by a current of nitrogen or CO_2 that passes through this compartment. After the cell is started, with external heat, the passage of the electric current maintains it at the proper temperature. The chlorine from the process is recovered as a by-product. The decomposition voltage of $MgCl_2$ is 3.25 volts, but from 5 to 8 volts are required. Under normal conditions a cell holding 100 pounds of electrolyte will yield from 26 to 28 pounds of metallic magnesium per twenty-four hours. The resulting magnesium may be further purified by fusion with sodium magnesium chlorate.

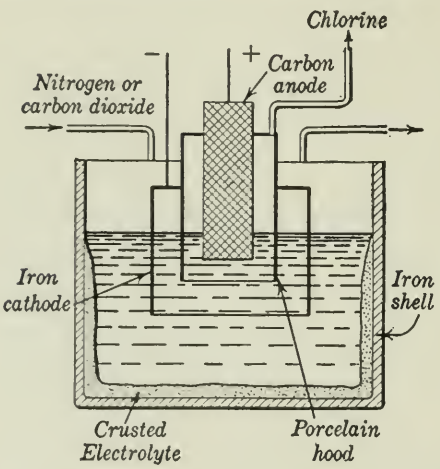

FIG. 149. Cell for electrolysis of magnesium chloride

MAGNESIUM OXIDE PROCESS

486. General. This process — a modification of the Hall-Héroult process for the reduction of aluminum — has been developed by the American Magnesium Corporation. Pure MgO is dissolved in a fused bath consisting of equal parts of MgF_2 and BaF_2, with sufficient NaF to maintain the requisite fluidity. The pure MgO can readily be obtained by the calcination of high-grade magnesite ($MgCO_3$).

487. Electrolysis. The cell used is shown in Fig. 150. It consists of a steel tank supported on cement blocks. The iron cathodes rest on copper bars on these blocks and enter the tank

through the bottom. The carbon anodes are supported on the framework of the tank and dip into the fused bath. Magnesium oxide as required is added to the fused mixture around the anodes. The top of the tank is covered with a hood for the collection of the reduced metal. This hood as well as the anode well are water-cooled. The magnesium is liberated at the cathode and rises through the bath to collect under the hood, from which it may be removed from time to time through the tap hole. The oxygen from the electrolysis burns at the carbon anodes. The bath is maintained at a temperature of 950° C. and at a specific gravity of 3.2. The voltage employed is from 9 to 16 volts. The metal thus obtained may be purified by fluxing or by sublimation.

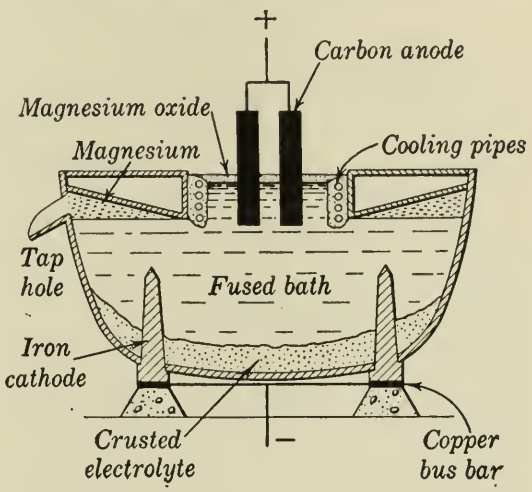

FIG. 150. Cell for electrolysis of magnesium oxide

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CHAPTER XIII

BISMUTH, TIN, ANTIMONY, ARSENIC, AND MERCURY

BISMUTH

488. Physical and chemical properties. Bismuth is a hard, brittle, crystalline metal having a reddish-white color and a bright, metallic luster. It has a specific gravity of 9.82. It melts at 271° C., boils at 1440° C., and has the property of expanding when it solidifies. It crystallizes in the rhombohedral system and, like most low-melting-point metals, develops quite large crystals on slow cooling. It is the most diamagnetic substance known. Its electrical conductivity is 1.8 (Ag 100). It is slowly acted upon by moist air, becoming covered with an iridescent film of the oxide. At higher temperatures than atmospheric it oxidizes readily in the air to Bi_2O_3. It is dissolved readily by HNO_3 and H_2SO_4. It combines directly with Cl, Br, and I.

489. Ores. Some bismuth is found in nature as the metal, the oxide, the carbonate, or the sulphide. Ores containing these compounds are generally low-grade and must be concentrated before the bismuth can be extracted. The most common source of bismuth is certain metallurgical by-products such as mattes, speisses, crude litharge, furnace bottoms, and anode slimes from the reduction and refining of lead.

490. Uses. Many salts of bismuth are used as medicines and in the X-ray examination of the internal organs. The pure metal has no use, being too brittle, but alloys of it with other metals are valuable in the arts. Those with other easily fusible metals are particularly valuable where low-melting-point alloys are desired for fuse plugs, electric cut-outs, sprinklers, etc. An alloy of Bi and Sn will melt at 232° C., while Wood's metal (50 per cent Bi, 25 per cent Pb, 12 per cent Sn, and 12.5 per cent Cd) melts at about 71° C. Certain bismuth compounds are also used in the staining of glass and in the manufacture of ceramic enamels. Bismuth alloys are used in making solders and dental amalgams, in silvering mirrors, and in electroplating.

491. Production, marketing, and prices. Owing to secrecy on the part of many of the producers it is difficult to give accurate statistics of the world's production of bismuth. Table L is an estimate of the production of the leading countries.

TABLE L. WORLD'S PRODUCTION OF BISMUTH (ORE AND METAL) IN METRIC TONS

	1915	1920	1921	1922	1923	1924	1925
United States	—	114	147	—	186	136	—
Australia	27	78	8	7	6	16	12
Bolivia	663	243	29	167	191	399	543
Peru	—	8	—	8	2	—	—
Spain	17	53	52	49	92	125	—

Metallic bismuth is sold in the form of bars weighing about 25 pounds. These are packed for shipment in wooden boxes containing 150 pounds. There are no standard specifications, but the following analysis shows the purity of the commercial metal:

	PER CENT
Ag	0.05
Pb	0.005
Cu	0.007
Fe	0.005
Zn	0.01
Bi	99.923

Metal that is to be used for the preparation of medicinal compounds must be free from arsenic and tellurium.

The price range in recent years is shown in Table LI. The control of the metal is virtually vested in the Bismuth Association, in turn controlled by a British syndicate, so that the price is largely an artificial one.

TABLE LI. PRICE OF METALLIC BISMUTH (NEW YORK)

YEAR	COST PER POUND
1910	$1.80
1915	2.45
1920	1.92
1921	1.82
1922	2.16
1923	1.90
1924	1.81
1925	2.50
1926	2.62
1927	2.17

Metallurgy

492. General. Bismuth may be reduced from its ores by wet methods, by fusion, or by a combination of these. For the purposes of this text only the following will be described, since practically all the bismuth is produced by some one of these processes: (1) fusion; (2) leaching; (3) electrolysis.

493. Fusion. Formerly considerable bismuth was produced from the native bismuth ores by simple liquation, but owing to the exhaustion of rich ores this has been superseded by the fusion process. The raw ore (if metallic) or the roasted ore (if the sulphide) is mixed with charcoal or coke and the necessary fluxes to yield a fusible slag and brought to a quiet state of fusion in either a crucible or a small reverberatory furnace. When fusion is complete the melt is cast into molds. After cooling there will be a separation into metallic bismuth, matte, speiss, and slag. The metal is sent on for further refining, the slag is a waste product, while the speiss and matte are returned to the process for re-treatment.

494. Leaching. This method is best suited to ores containing bismuth in the oxidized condition. The ore is crushed to about 60 mesh and treated, in stoneware jars, with HCl. Metallic bismuth or alloys are best brought into solution with HNO_3, H_2SO_4, or aqua regia. The solution is heated and water is added until the white bismuth oxychloride just begins to precipitate; the solution is then siphoned off, water is added to complete the precipitation, and a separation is effected. This oxychloride is washed with water, dissolved, and re-precipitated several times in order to remove the lead. It is then passed through filter presses, dried, and smelted with C, Na_2CO_3, and $CaCO_3$ to the metal. This metal is usually too impure to be used directly.

495. Electrolysis. Alloys of bismuth have been successfully treated by electrolysis in an electrolyte of lead fluosilicate and hydrofluosilicic acid. The anodes are plates of the cast alloy; the cathodes are pure lead. In the electrolysis pure lead is deposited on the cathode, while the bismuth remains behind on the anode. This anode is washed and remelted. The process does not yield a pure bismuth, but one containing ordinarily from 3 to 10 per cent of Pb.

496. Refining of bismuth. Bismuth produced by the fusion method contains from 4 to 10 per cent of impurities. Chief among these are Pb, As, Sb, S, Se, Te, Fe, Ag, and Au. Such metal is not suitable for industrial purposes and must be further refined. While the refining can be carried out by fusion, electrolysis, or wet methods, owing to the expense the last method is seldom used.

Because of the complexity of the fused mixture it is often necessary to make several fusions, each under different conditions and with different fluxes, in order to remove the impurities. For example, fusion with sulphur will remove the Cu and some of the Ag as matte; fusion with caustic soda removes Te, Se, As, Zn, S, and Sb; fusion with Zn removes Au and Ag. Final purification may be effected by repeated crystallizations, as in the Pattinson process. In this way it is comparatively easy to produce a metal containing as much as 99.95 per cent of Bi.

Electrolysis is carried out in an electrolyte of bismuth chloride and HCl in a porcelain container. The anodes are impure bismuth; the cathode is sheet lead covering the bottom of the cell. The anodes are covered with cotton duck. The bismuth collects on the cathodes and is removed from time to time, washed, fused with caustic soda, and cast into bars. This treatment does not remove all the Te or any of the Ag or Au.

Tin

497. Physical and chemical properties. Tin is a soft, silver-white metal with a brilliant luster. It is very malleable at ordinary temperatures, but when exposed for long periods of time to temperatures below the freezing point of water it changes into a grayish-white powder. It cannot be drawn into wire. It has a specific gravity of 7.28, melts at 232° C., and boils at 2200° C. It is not acted upon by either air or water at ordinary temperatures, but at higher ones it is oxidized to stannic acid. Tin forms alloys with many metals. It is attacked by the common inorganic acids, both dilute and concentrated, and by the stronger basic hydroxides.

498. Ores. Practically all the world's tin is obtained from the mineral cassiterite (SnO_2). Most of this occurs in placer gravels, very little being found in the form of lode deposits.

There are no deposits of any extent or richness in the United States. We are entirely dependent for our supplies upon the Straits Settlements, Bolivia, the Dutch East Indies, and China, which countries produce about 80 per cent of the world's supply. The world's production in recent years is shown in Table LII.

TABLE LII. WORLD'S PRODUCTION OF TIN (IN TONS OF 2240 POUNDS)*

YEAR	BOLIVIA	DUTCH EAST INDIES	MALAY STATES	GREAT BRITAIN	CHINA	SOUTH AFRICA	ALL OTHERS	TOTAL
1910 .	1,003	15,871	57,490	4,874	6,510	—	30,011	115,759
1915 .	21,544	19,255	46,765	4,968	7,995	2,056	24,289	126,872
1920 .	27,821	21,181	34,935	3,065	10,566	1,429	23,100	122,097
1921 .	18,804	26,382	34,490	679	11,200	720	21,187	113,462
1922 .	31,616	29,278	35,286	370	12,435	470	20,889	130,344
1923 .	29,777	29,138	37,649	1,021	8,727	884	23,058	130,254
1924 .	31,553	31,558	44,043	1,986	6,858	1,150	23,199	140,347
1925 .	32,083	32,749	45,925	2,339	8,789	1,142	21,734	144,761
1926 .	32,113	33,006	45,946	2,327	6,538	1,087	22,851	143,868

499. Uses. The most valuable property of tin is its resistance to corrosion by air, water, and weak acids. It therefore makes a valuable coating material for iron when used for food containers, kitchen utensils, roofs, etc. It is also an important alloying agent in the manufacture of solders, bronzes, bearing metals, and pewter. Tin foil finds considerable use in the wrapping of certain food products. Tin salts are frequently used for weighting silks. Table LIII indicates the various uses in the United States.

TABLE LIII. CONSUMPTION OF TIN IN THE UNITED STATES

	LONG TONS	PER CENT
Tin and terneplate	27,600	36.20
Solder	17,000	22.30
Bearing metal	10,800	14.16
Brass and bronze	4,800	6.29
Collapsible tubes	2,100	2.75
Foil	4,000	5.24
White metal	1,750	2.30
Tinning metal	1,900	2.50
Chemicals	1,700	2.22
Britannia ware	1,000	1.31
Miscellaneous	3,607	4.73
Total	76,257	100.00

* Mineral Industry.

500. Marketing and prices. Tin is sold in the form of pigs weighing about 100 pounds each. Two classes of tin are recognized in the domestic market: Standard, or Straits, tin, containing 99.75 per cent of Sn or more; and the 99 per cent grade.

The price of tin fluctuates between rather wide limits. Whether this is due to attempts on the part of foreign combinations to fix the price or to fluctuations in the domestic consumption it is impossible to say. Since the tin reserves are very limited and the mines are held by a few large combinations, the former seems more likely. At any rate no other common metal exhibits such erratic behavior in this respect as is indicated by the price tabulation of Table LIV.

TABLE LIV. PRICE OF TIN IN NEW YORK

	CENTS PER POUND
1895	14.05
1900	29.90
1910	34.23
1915	38.59
1920	48.73
1921	28.57
1922	31.83
1923	41.80
1924	49.67
1925	56.79
1926	63.62
1927	62.75

METALLURGY

The steps involved in the production of relatively pure metallic tin from the oxide ore are as follows: (1) concentration; (2) blast-furnace smelting; (3) reverberatory smelting; (4) treatment of the slag; (5) refining.

501. Concentration. The ore is almost never found in deposits rich enough for direct smelting. More often the cassiterite is mixed with gangue and may contain many harmful impurities. At the mines some form of concentration, water gravity, or oil flotation is employed to bring the material up to the standard grade — 60 per cent Sn. If a lower grade than this is used in smelting, both the cost of the operation and the slag losses are higher. A higher grade than this is difficult to attain without excessive losses in the concentrating process. Other methods

of concentration that have been attempted are leaching, roasting, mechanical concentration, and chloridizing. Concentration serves to remove the gangue, while roasting or chemical treatment serves to remove S, As, Fe, Cu, Bi, Zn, and other harmful impurities. All such treatment aims at the production of as high-grade a product as possible for subsequent smelting.

502. The blast furnace. The blast furnace used to be the only means employed to reduce the oxide, but today it has been replaced to a considerable extent by the reverberatory furnace. The reduction of the oxide is not a difficult process; witness the fact that students carry it out in blowpipe analysis in the laboratory. The difficulty and the low recovery of tin in the process result from the fact that tin oxide combines readily with the silica of the ore or flux to form tin silicate, which enters the slag and may be lost. Even under the best of smelting conditions this loss is a high one, and all primary slags contain from 10 to 20 per cent of Sn and must be re-treated. The blast furnaces used at present are small water-jacketed ones, similar to those used in the reduction of lead ores. The slag and metallic tin are collected in a forehearth, or settler. The crude tin is sent on to the refinery, and the primary slag is re-treated, at least once, in order to recover some of the tin.

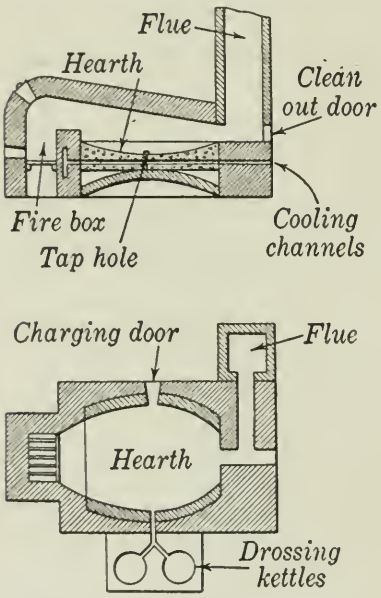

FIG. 151. Reverberatory furnace (tin)

503. Reverberatory smelting. Most of the tin at present is produced in reverberatory furnaces, since this type of appliance is easier to operate and yields much cleaner slags and less flue dust. The latter advantage is an important one, for tin is a valuable metal and an increasing proportion of the concentrates is in the form of fine dust which may be easily carried over into the flue chambers and lost. A typical tin reverberatory furnace is shown in Fig. 151. In general they are much smaller than the copper furnaces. The furnace shown has a hearth 15×9 feet and will treat about 5 tons of charge per

twenty-four hours. The fine ore is mixed with from 15 to 20 per cent of anthracite fines and the proper fluxes to produce a fusible slag of the desired silicate degree. It is brought slowly to a temperature of from 1200° to 1300° C. At the end of from ten to twelve hours fusion is complete and the reduced metal and slag is tapped from the furnace into a settler. The molten tin is cast into pigs of 75 pounds each, and the slag is cast into cakes or slabs which are later broken up for re-treatment. There must be an elaborate dust-collecting apparatus for the flue dust and volatile tin compounds which are easily formed.

504. Treatment of slags. Primary slag, from either the blast furnace or the reverberatory, contains too much tin (Sn, 10 per cent; Fe, 15 per cent) to be discarded as a waste product. The slag is crushed and mixed with large amounts of carbonaceous reducing material, limestone, and scrap iron. The limestone and iron serve to break up the tin silicates; the carbon, to maintain a reducing atmosphere in the furnace. Under proper conditions the slag from the re-treatment process will contain less than 1 per cent Sn. The reduced tin, termed *hard head*, contains a large amount of iron and other impurities, and hence must be refined for market. The smelting of slags is at best a difficult operation. To keep the loss of tin within reasonable limits it is necessary to have skilled workmen and a very close control of the furnace operations.

505. Refining. Both fire and electrolytic methods have been used for the refining of tin. Electrolysis was employed at some of the domestic smelters during the World War, but these have since closed down, owing to European competition.

Fire refining consists of two operations: (1) liquating, or sweating, and (2) boiling, tossing, or poling. Either one or both of these operations may be employed, depending upon the character and amount of the impurities. Liquating is carried out in a small reverberatory furnace (3 feet wide and 5 feet long). The hearth of this furnace slopes toward one side, where there is a tap hole. The bars of tin are piled at the upper side of the furnace, melted, and kept at a temperature just above the fusing point of the alloy. The tin melts readily, while most of the other metals and compounds entrained in it remain solid. The refined tin is tapped from the furnace and cast into ingots, while the dross collects on the surface of the metal and may be

re-treated from time to time by raising the temperature of the furnace (sweating). Finally, when no more tin can be collected by this means, the dross is skimmed off and returned to the first smelting furnace. Most of the Fe, As, Sb, and Cu go into the dross, while Pb and Bi remain in the tin. The boiling

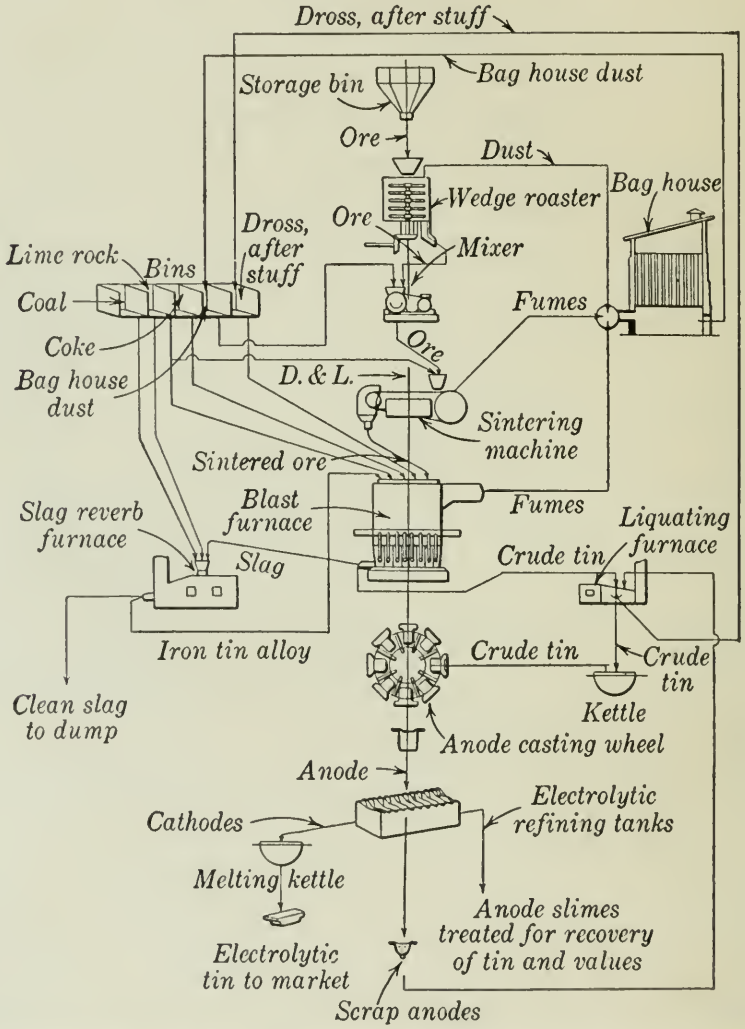

FIG. 152. Flow sheet of tin-blast-furnace smelting process

operation is similar to the fire refining of copper. The tin, in a cast-iron kettle, is brought to a temperature considerably above its melting point and then stirred with a green-wood pole. The moisture and the volatile hydrocarbons from the wood serve to stir and agitate the metal. It is thus exposed to the action of the atmosphere, and the impurities are oxidized. The operation may be carried on for several hours; at the end

of that time the desired degree of purity is reached. The impurities collect on the surface as a dross and may be removed. The tossing operation accomplishes the same thing in a different way. The tin is taken up in small ladles and poured back into the kettle. In passing through the air at this elevated temperature the impurities are oxidized. Iron may be almost completely removed, and the other impurities greatly reduced.

506. Electrolysis. By this means it is possible to produce tin of a very high degree of purity, but at the present time, owing to economic conditions, electrolysis cannot compete with the fire methods. The electrolyte employed is hydrofluosilicic acid with small amounts of sulphuric acid, cresylic acid, and glue. The tin will dissolve in this to the extent of about 4 per cent. The anodes are cast from primary tin, the cathodes are starting sheets about $\frac{1}{8}$ inch thick. The tanks and apparatus used are similar to those used in the electrolytic refining of copper.

The flow sheet of a domestic tin smelter is shown in Fig. 152.*

ANTIMONY

507. Physical and chemical properties. Antimony is a silvery white metal, lustrous, hard, and brittle. It has a specific gravity of 6.62. It melts at 630° C. Like phosphorus and arsenic it occurs in several allotropic forms. Besides the metallic antimony of commerce there is explosive antimony, black antimony, and yellow antimony. It is not acted upon by dry air but is slightly tarnished by moist air. It burns in air when heated to a sufficiently high temperature. It is dissolved by the strong acids. With many of the common metals it forms alloys of commercial importance.

508. Ores. The chief ore of antimony is stibnite (Sb_2S_3). Rich deposits of this mineral are found in China, Mexico, and Bolivia, the first-named country being the chief source of supply. We have no deposits of any importance, most of our domestic metal being obtained as a by-product in treating the flue dust, drosses, and slags formed in the smelting of certain copper and lead ores. Usually this antimony is not reduced to the pure metal but is marketed in the form of antimonial lead (about

* *Transactions of the American Society of Mining and Metallurgical Engineers*, Vol. LXX, p. 404.

15 per cent Sb). This commands a ready sale and is a convenient form for use in alloying. The crude sulphide of antimony is called *crude antimony, liquated antimony,* or *needle antimony.* The refined metal is called *regulus.*

509. Uses. The chief use of antimony is as an alloying agent. It alloys readily with most of the nonferrous metals, makes them harder, and confers on them the property of sudden expansion on solidifying. This property is taken advantage of in type and bearing metal. *Antimony white* (Sb_2O_3) is in common use as a pigment. The red trisulphide is used as a filler and in vulcanizing rubber. In the manufacture of storage batteries, vitreous enamels, shrapnel, and hard lead, antimony or some of its compounds is essential. Solutions of the trichloride in creosote or benzol are used as fire preventives and wood-preservers. The trisulphide is used in making safety matches as well as the compound on which these are scratched.

510. Production. The world's production of antimony is given in Table LV. There is no antimony mining and no domestic smelting industry in the United States. The small amount of antimony produced in recent years has been a by-product in the treatment of the flue dust and fume from copper and lead smelters. Practically all the imported metal comes from China. Our consumption in ordinary times is in the neighborhood of 10,000 tons per year.

TABLE LV. WORLD'S PRODUCTION OF ANTIMONY (IN METRIC TONS)

	1911	1915	1920	1921	1922	1923	1924	1925	1926
United States	—	1,760	—	—	4	9	33	33	24
Mexico . .	4,554	200	1,572	45	457	490	775	1,399	1,200
Bolivia . .	344 *	9,859	588	336	185	312	751	1,850	1,568
France . . .	32,267 *	893	1,413	1,118	814	437	873	795	910
Algeria . .	—	2,740	1,000	103	530	500	236	880	840
China . . .	15,211 †	23,357	13,109	14,752	14,316	14,244	13,168	19,040	28,848
All others .	‡	4,413	2,066	1,238	2,318	1,817	1,817	1,230	1,224
Total . .	‡	43,222	19,748	17,592	18,624	17,809	17,653	25,227	34,614

* Ore. † Ore and metal. ‡ Not available.

511. Marketing and prices. The metal is marketed in the form of slabs weighing from 30 to 40 pounds. The market unit is a case of 224 pounds net. The minimum grade is 99 per cent Sb,

but certain users who demand it can obtain a metal of a higher grade. *Star antimony*, a term frequently encountered, refers to the starlike crystals of the pure metal which many users demand. Such preference is more a matter of custom than anything else, for the presence of these stars really has little relation to the purity.

The price range of the metal in recent years is shown in Table LVI.

TABLE LVI. PRICE OF ANTIMONY IN NEW YORK

YEAR	CENTS PER POUND
1910	7.39
1915	29.64
1920	8.49
1921	4.96
1922	5.47
1923	7.90
1924	10.84
1925	17.50
1926	15.99
1927	12.39

METALLURGY

512. General. There are two oxides of antimony: the nonvolatile tetroxide (Sb_2O_4) and the volatile trioxide (Sb_2O_3). The reduction of antimony from its ore can be conveniently divided into five steps, one or more of which may be omitted, depending upon the grade of the ore and the use to which the finished metal is to be put. These steps are (1) liquation of the crude ore; (2) preparation of the tetroxide (Sb_2O_4); (3) preparation of the trioxide (Sb_2O_3); (4) reduction in reverberatory furnaces; (5) reduction in blast furnaces.

513. Liquation of the crude ore. The crude ore may contain from 15 to 90 per cent of the sulphide. The higher grades may be marketed directly, but the lower grades must be concentrated before they can be smelted. This is a simple process carried out either in pots or in small reverberatory furnaces. The ore is crushed to about $\frac{3}{4}$ inch in diameter, charged into the furnace, and brought slowly to the proper temperature for liquation. If the temperature is too high, some of the Sb_2O_3 is volatilized; if it is too low, a considerable amount of sul-

phide may be left behind in the residue. Under the proper conditions the stibnite will melt and collect in the pot or furnace. A recovery of from 80 to 90 per cent of the antimony may be expected in the form of relatively pure needle antimony.

514. Preparation of the tetroxide. The preparation of the stable Sb_2O_4, the next step in the reduction to the metal, is carried out by means of an oxidizing roast in a reverberatory furnace. The furnace is maintained at a temperature of about 350° C., and an excess of air is allowed to enter. Under these conditions, with constant stirring, the mass will be converted almost entirely into the tetroxide (Sb_2O_4). If the temperature rises too high, a part is volatilized as the trioxide (Sb_2O_3). The material to be roasted must be fairly pure; otherwise the sulphur or other foreign elements will form antimonides, sulphates, and arsenates, and will contaminate the product. The roasted ore will have a reddish color in the furnace and a gray color when cool. The operation is entirely a hand one and requires considerable skill to prevent the sintering or fritting of the charge or a loss through volatilization. A furnace 40×6 feet will roast about 1 ton per twenty-four hours and recover about 92 per cent of the antimony as tetroxide.

515. Preparation of the trioxide. The preparation of the trioxide requires a slightly higher temperature, a restricted supply of air, and a rather elaborate condensing system. The advantages of the method are as follows:

1. The material is pure enough and in the proper form for direct marketing.
2. The residues may be treated for precious metals.
3. The loss of antimony is less.
4. The method is better suited to low-grade ores.
5. Arsenic is eliminated.

The process in common use today, shown in Fig. 153, is one developed by Herrenschmidt. It consists of a furnace, condensers, and an absorption plant. The ore, crushed to about $\frac{1}{4}$ inch and containing from 10 to 20 per cent of Sb, is mixed with from 5 to 10 per cent of charcoal and charged upon the grates of the roasting furnace. At a temperature of about 400° C. the Sb_2S_3 is oxidized to the volatile trioxide and is drawn over into the condensation pipes by means of the two fans. Water

is admitted at the top of the coke tower, and this, trickling down through the tower, serves to condense any fume which may have escaped the condensation pipes. The recovery of antimony, dependent largely upon the skill of the operator, is about 90 per cent. It is difficult to volatilize ores containing more than 30 per cent of Sb, owing to the fritting or sintering of the charge. The ideal ore should contain from 15 to 25 per cent of Sb.

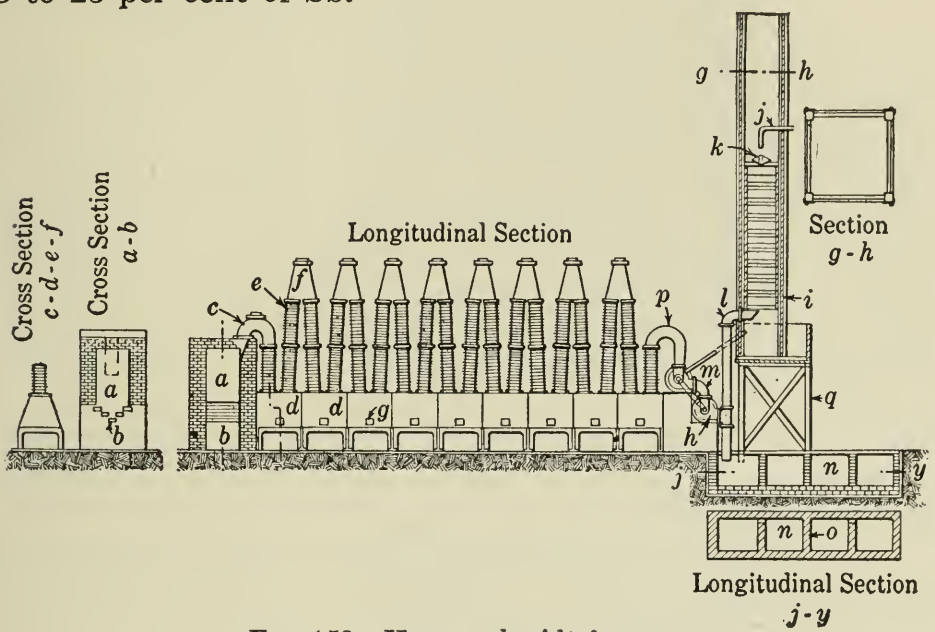

FIG. 153. Herrenschmidt furnace

516. Reduction in reverberatory furnaces. A reverberatory furnace for the reduction of antimony is shown in Fig. 154. It differs from the ordinary reverberatory in the size and shape of the hearth. The process consists of the simple reduction of the metal with carbon. The charge is made up largely of roasted ore, NaCl, Na_2CO_3, and charcoal, with small amounts of flue dust, residues, and Glauber's salt, as the judgment of the operator dictates. In the fusion the antimony is reduced and collects in the bottom of the furnace, while the soda unites with the gangue to form a slag which in turn absorbs any foreign metals as sulphides or chlorides. Connected with the furnace is usually an elaborate condensation apparatus to recover any volatile trioxide which may have been formed during reduction. The recovery of antimony is rather low, ranging from 88 to as low as 60 per cent.

517. Reduction in the blast furnace. The furnaces used are small ones of rectangular cross section, similar to those used in the treatment of lead ores. The antimony ores, if of too low a grade, are concentrated to a 25–40 per cent product. This ore is then roasted, mixed with limestone and iron oxide to give a proper slag and with coke as a reducing agent, and

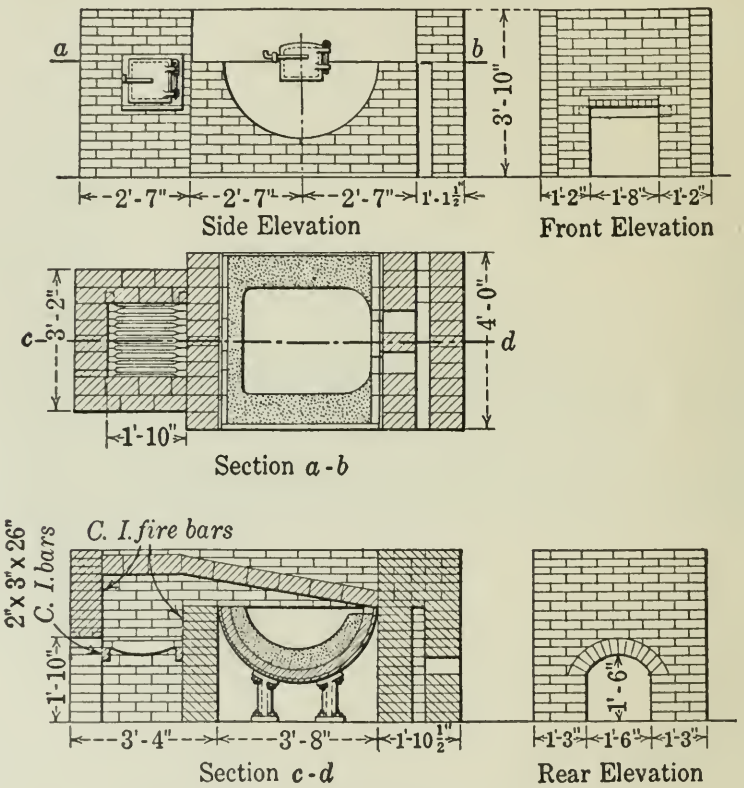

FIG. 154. Small reverberatory furnace

smelted in much the same way as a lead ore. The metal and slag are collected in a forehearth, where the separation takes place. The recovery of antimony may run as high as 98 per cent. Sometimes a considerable amount is volatilized, so that an elaborate bag house or condensation equipment must be provided. The cost of the apparatus is the chief disadvantage of this process.

518. Refining of the impure metal. Antimony produced by any of these processes is likely to contain S, Fe, As, Cu, or Pb. The refining operation is usually carried out in a small reverberatory furnace holding about one ton of charge. This

charge consists of impure antimony, Na_2CO_3, and coke or charcoal. Arsenic is removed as the oxide either in the slag or up the flue. Copper and lead are scorified and enter the slag. These slags will contain large amounts of Sb and are returned to the process. The refined metal will contain from 99.6 to 99.9 per cent of Sb.

ARSENIC

519. Physical and chemical properties. Like phosphorus, the metal arsenic may exist in more than one form. In its stable form it is a steel-gray, brittle metal with a specific gravity of 5.7. If this metal is sublimed, there is obtained a black or gray vitreous form with a specific gravity of about 4.6. The first form crystallizes in the rhombohedral system, while the latter is amorphous. A third variety is yellow arsenic, formed at $-70°$ C. from carbon disulphide solution. This arsenic crystallizes in the cubic system.

The ordinary metallic arsenic volatilizes at 450° C. and at atmospheric pressure without first melting. Under increased pressure it melts at 830° C. It is not attacked by dilute acids. It is dissolved by strong HNO_3 or H_2SO_4.

520. Ores. The chief ores of arsenic are arsenopyrite (FeAsS), orpiment (As_2S_3), and realgar (As_2S_2). Deposits containing these minerals are found in Nova Scotia, Japan, and the United States. Most of our arsenic — enough in normal times to supply the demand — is obtained as a by-product in the smelting of copper, lead, and silver ores, where it is recovered in the form of flue dust and speiss.

521. Uses. Metallic arsenic is added to the lead used in the manufacture of shot in order to prevent the formation of imperfect shot in the tower. It serves to toughen copper and bronze. It is used a great deal in rat poisons, insecticides, sheep dip, and weed-killers. In the last few years the industry has been greatly stimulated by the use of calcium arsenate in fighting the boll weevil, which has attacked the cotton crop of the South. In electroplating, arsenic tends to give an oxidized finish to brass articles. Many organic compounds of the metal have value as medicines. The pure metal, as such, has no engineering or structural use.

522. Production. The world's productive capacity in arsenic-refining plants has been estimated as follows:

	Short Tons per Year
United States	20,000
Mexico	6,000
Germany	4,000
Canada	3,500
England	3,000
Japan	3,000
France	2,500
Belgium	1,500
Greece	1,000
All others	2,000
Total	46,500

It is likely that 40,000 tons is about the largest annual production at present available, and this could not be maintained for long, since the reserves of rich ore are very limited. It is a vital question for us, however, in our war upon the various pests now attacking our crops. The actual production of the United States in recent years is given in Table LVII. The sudden increase in 1920 is due to the use of calcium arsenate in fighting the boll weevil in the South.

Table LVII. Production of White Arsenic in the United States

Year	Short Tons
1910	1,497
1915	5,498
1920	11,502
1921	4,786
1922	10,027
1923	14,271
1924	19,242
1925	11,816
1926	8,761

523. Marketing and prices. Since most of the domestic arsenic is used in the manufacture of insecticides, weed-killers, spraying compounds, etc., the demand for it is an extremely variable one. It has fluctuated from 3000 to 25,000 tons per year. It follows, then, that the price should also be variable. This is borne out by the figures given in Table LVIII, which shows the price range during recent years.

TABLE LVIII. PRICE RANGE OF WHITE ARSENIC IN NEW YORK (IN CENTS PER POUND) *

YEAR	HIGH	LOW
1915	7.0	3.5
1920	16.0	9.0
1921	10.0	5.5
1922	15.5	6.0
1923	16.0	8.25
1924	13.5	6.0
1925	6.0	3.0
1926	3.5	2.75
1927	4.0	3.75

The metal is marketed in the form of its compound, white arsenic (As_2O_3). White arsenic must contain not less than 99 per cent of As_2O_3. Many consumers also have rather exacting specifications regarding color and fineness. It is usually put up in casks containing about 450 pounds each.

METALLURGY

524. Preparation of metallic arsenic. The reduction of metallic arsenic from the trioxide is a simple process, and by this means metal of a 99.5 per cent grade may be obtained with relative ease. A charge consisting of 25 per cent of powdered charcoal and 75 per cent of As_2O_3 is intimately mixed in a rotary mixer. This material is then charged into the reduction furnace. This consists of a steel pipe about 2 inches in diameter and 6 feet long, surrounded by fire brick and inclosed in a steel jacket. It is heated by gas. The charging end of the furnace is closed by means of a water-cooled cover and the other end is connected with a condensing system. The metallic arsenic collects in the condensing pipe and may be removed with chisels, any uncondensed fume passing out through a water seal.

525. Preparation of white arsenic. Nearly all the arsenic now used in industry appears on the market in the form of arsenious oxide (As_2O_3). In fact, the name *arsenic*, as ordinarily used, refers to the oxide and not to the pure metal. Whether the white arsenic is made from flue dust, calcine, metallurgical by-product, or crude ore, the process is, in principle, much the

* Mineral Industry.

same. It is divided into two distinct steps when the pure refined product is desired: (1) the production of a crude white arsenic (about 70 per cent pure), and (2) the refining of this crude material to a 99 per cent product. The scheme of treatment as carried out at one of our large metallurgical plants is shown in Fig. 155.

The plant consists of four 16-foot MacDougall roasters. Roaster *a* is constructed in the usual way. Material containing as high as 50 per cent of As_2O_3 is charged on the top hearth and passes through the furnace at a rate of 30 tons per twenty-four hours. By means of external fire boxes the temperature of the furnace is maintained at about 650° C. The residue contains

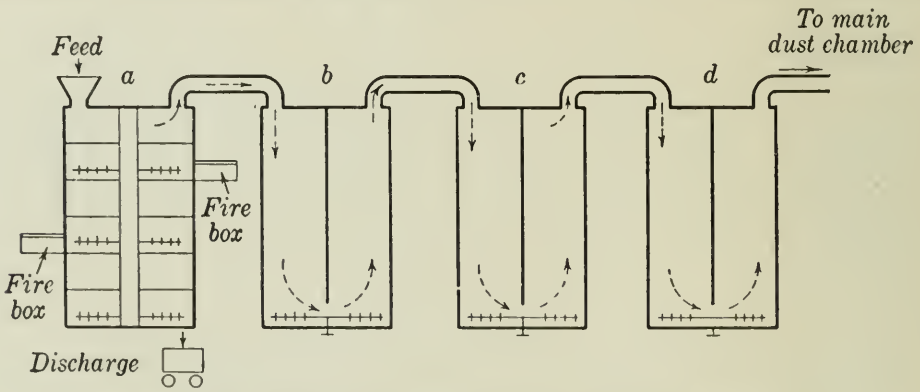

FIG. 155. Plant for precipitation of crude arsenic

about 15 per cent of As_2O_3 and is sent back to the smelter for re-treatment. From furnaces *b*, *c*, and *d* the hearths and all except one of the sets of arms are removed and a vertical partition built, dividing the furnace into two compartments. These furnaces serve as condensing units, the gas from *a* entering at the top and passing through the partition at the bottom and out at the top. The bottom sets of arms are operated from time to time to remove the arsenic as it collects. This crude arsenic will, under ordinary conditions, contain 90 per cent of As_2O_3.

The refining plant consists of a reverberatory furnace with a hearth 27 feet long and 12 feet wide. It differs from the ordinary type in that the hearth is built of cast-iron plates and there are two fire boxes, one at the back and the other at the front. The gases from the former pass under the hearth and over the top of it, while those from the latter pass only over the top. The charge (8 tons per twenty-four hours) is dropped through openings in the roof and is worked, by means of rabbles, through the

side doors. The residue is cleaned out and returned to the crude furnace every two days. A temperature of 550° C. is maintained, and about 80 per cent of the arsenic is recovered.

The condensing chambers for the sublimation of the white arsenic are called kitchens. Each chamber is 225 feet long and is divided into thirty-nine compartments. In the first chamber are collected the flue dust and foreign elements from the ore. The gases cool, as they pass through the chamber, from 300° C. at the furnace end to 100° C. at the exit end. Most of the arsenic is caught at from 120° to 180° C. The first few kitchens contain arsenic of a 95 per cent grade, which must be sent back for refining. The succeeding ones yield a 99.9 per cent product for shipment. The gases coming from the kitchens pass through a bag house which yields a product, containing about 90 per cent As_2O_3, that is either sold as crude white arsenic or sent back to the reverberatory furnaces for re-treatment.

FIG. 156. Arsenic kitchens

MERCURY

526. Physical and chemical properties. Mercury is the only metal that is liquid at ordinary temperatures; it does not freeze above −39° C. The pure metal freezes at −38.87° C. and boils at 357° C. Mercury possesses a very high surface tension, so that small drops of it tend to assume an almost perfectly spherical form.

Mercury forms with many other metals a series of alloys known as amalgams. Thus, if small amounts of Na, Ag, or Au are added to mercury, these are dissolved, leaving the alloy still liquid. Increasing amounts of these metals cause the alloy to become solid. Such amalgams can easily be decomposed by the application of heat. The separation of gold from rock is accomplished on a commercial scale by taking advantage of this property.

The metal is not attacked by either dilute HCl or H_2SO_4. It is dissolved by hot concentrated H_2SO_4 or HNO_3. The sulphide is easily decomposed by the application of heat.

527. Ores. Mercury is found in nature as cinnabar (HgS), a soft, bright-red mineral. It is very seldom found native. We have in this country small, scattered deposits of the ore averaging about 0.4 per cent Hg, but in Spain, Idria, and Tuscany there are very extensive deposits containing as high as 15 per cent of Hg. Our mines cannot possibly compete with such ores and the cheap labor available in those countries.

528. Uses. As the only metal that is liquid at ordinary temperatures, mercury has unique and peculiar uses. Mercury fulminate ($HgC_2N_2O_2$) is an essential constituent of all caps for the detonating of high explosives. Its use in barometers, thermometers, and pressure gauges is familiar to everyone. It expands more than any other liquid on being heated, so that it is valuable in thermostats. Recently it has been used a great deal in electrical circuit breakers and switches. The manufacture of felt and pigments also consumes small tonnages. Other uses are indicated in Table LIX.

TABLE LIX. USES OF QUICKSILVER (ESTIMATED)*

	FLASKS
Drugs and chemicals	8,500
Fulminate	4,850
Vermilion	3,130
Marine paint	3,000
Electrical apparatus	2,700
Felt manufacture	1,700
Amalgamation	850
Instruments	630
Boiler compounds, cosmetics, etc.	1,000
	26,360

* J. E. Spurr and F. E. Wormser, Marketing of Metals and Minerals.

529. Marketing, production, and prices. Domestic mercury is marketed in a unit known as the *flask*. This is a cast-iron bottle holding 75 pounds. The European flask holds 34.5 kilograms. Owing to market manipulation the price fluctuates between wide limits, as indicated in Table LX.

TABLE LX. AVERAGE PRICE OF QUICKSILVER IN NEW YORK

YEAR	COST PER 75-POUND FLASK
1910	$47.06
1915	87.01
1920	81.12
1921	45.46
1922	58.95
1923	66.70
1924	69.76
1925	83.13
1926	91.90
1927	118.16

The production of this metal, as indicated in Table LXI, is concentrated in Italy and Spain. In these countries there are very rich deposits and cheap labor, so that only our most favored producers can compete with them in the domestic market. Before the World War the Rothschilds of England controlled the entire Spanish output and, by a frequently renewed agreement, most of the Italian and Austrian metal. Since the war, however, this has been changed, so that now the Spanish and Italian governments control their respective outputs. It is small wonder, then, that the price of the metal exhibits such erratic behavior.

TABLE LXI. WORLD'S PRODUCTION OF QUICKSILVER (IN METRIC TONS)

YEAR	AUSTRIA	ITALY	MEXICO	SPAIN	UNITED STATES	OTHER COUNTRIES	TOTAL
1909 . . .	637	771	200	1393	713	180	3894
1915 . . .	760	985	94	1222	716	304	4081
1920 . . .	—	1401	77	861	455	118	2912
1921 . . .	—*	1071	46	635	216	167	2135
1922 . . .	—	1541	42	1318	217	125	3243
1923 . . .	—	1656	45	1144	270	157	3272
1924 . . .	—	1595	37	899	342	210	3083
1925 . . .	6.1	1834	39	1277	312	32	3500
1926 . . .	—†	71	45	1594	260	—†	—†

* Idria mines ceded to Italy after 1918. † Not available.

Metallurgy

530. General. Nearly all mercury is reduced by distillation methods, since the sulphide breaks up on heating in the presence of air, thus:

$$HgS + O_2 = Hg + SO_2.$$

The character of the apparatus, but not the principle, varies at the different plants. For the purpose of this text only three types of furnaces will be described: (1) retorts; (2) the Scott furnace; (3) rotary furnaces.

531. Retorts. The Johnson-McKay retort consists of a cast-iron pipe, 12 inches in diameter and 6 feet long with a wall 1 inch in thickness. One end is bell-shaped, so that lids may be fixed in position and made gas-tight with clay or cement. The other end is connected by means of a 3-inch pipe with the condensing system. The pipe is given a slight slope toward the condensing end for the purpose of draining the mercury. From six to twelve of these are grouped together to form a bank and inclosed in brickwork, so that a temperature of from 400° to 800° C. can be maintained in the retort. If much sulphur is present, lime is charged with the ore to promote the decomposition of the cinnabar, thus:

$$4\,HgS + 4\,CaO = 4\,Hg + 3\,CaS + CaSO_4.$$

Each pipe will hold about 200 pounds of charge, so that the capacity of a 12-pipe bank is only from 2 to 4 tons per twenty-four hours. For this reason the retort is unsuited to anything except concentrates or very high-grade ore.

532. The Scott furnace. The Scott furnace, since its invention in 1876, has been widely used in this country for the treatment of mercury ores. Such a furnace is shown in Fig. 157. The dried ore, crushed to about $1\frac{1}{2}$ inches, is fed in at the top and pursues a zigzag course down through the furnace, passing over a series of tile shelves. Each one of these reverses the course of the ore, so that fresh surfaces are exposed to the action of the heated gases passing across the shelves from a fire box located at the side. Since wet or sticky ores often give trouble by lodging on the shelves, the waste heat from the furnace is often used to dry the ore. After the ore has passed through the furnace (the time of contact depending upon the character of the ore),

it is drawn off at the bottom into cars and taken away. The mercury decomposed and volatilized by the heat is carried away by the gases of combustion to an elaborate condensing system made of tile pipe. There the mercury vapor is condensed and the metallic mercury recovered by periodic clean-ups. The slope of the shelves is slightly greater than the angle of repose of the ore, so that when one car of burned ore is withdrawn from the bottom of the furnace the ore on all the shelves drops and leaves room for another car at the top. Usually there is a gas seal at the top of the furnace, for the mercury vapor escapes very easily, not only causing a serious loss but endangering the health of the workmen. Such a furnace will treat about 40 tons per twenty-four hours and consumes two cords of wood.

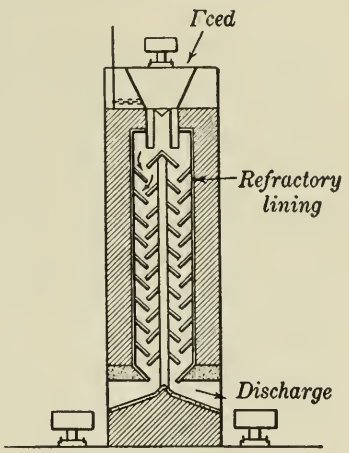

FIG. 157. Scott furnace

533. Rotary furnace. The rotary furnace is similar to the kilns used in the burning of cement. It is lined with refractory material, and sealed joints are provided at the feed end, discharge end, and fire box to prevent the escape of mercury vapor. These furnaces are from 2 feet in diameter and 30 feet long to 5 feet in diameter and 75 feet long. The ore, crushed to $1\frac{1}{2}$ inches, is fed into the furnace by means of a screw or shove conveyor. Oil, gas, coal, or wood may be used as fuel. The fume from the furnace passes first into a dust chamber and then into a tile-pipe condensing system. The advantages claimed for this type of furnace are lower cost of installation and operation, fuel economy, higher extraction, and greater ease in starting and stopping.

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CHAPTER XIV

MANGANESE, CHROMIUM, NICKEL, AND COBALT

MANGANESE

534. Physical and chemical properties. Manganese is a reddish-gray metal with a specific gravity of 7.4. The melting point of the pure metal is 1260° C. When pure it is not so hard as glass, but the commercial metal, with considerable C and Si, will scratch steel. At normal temperatures it is not attacked by the atmosphere, but at higher ones it is rapidly oxidized. It combines readily with S and O. It is easily dissolved by all dilute acids.

535. Ores. The most important mineral containing manganese is pyrolusite (MnO_2), although manganite ($Mn_2O_3 \cdot H_2O$), braunite (Mn_2O_3), and rhodocrosite ($MnCO_3$) are also sources of the metal. The high-grade ore may contain as much as 35 per cent of Mn, but more often it is so low-grade that it must be concentrated before being smelted. Since 1918 the following classification of ores has been in effect:

1. High-grade ores with 35 per cent or more of manganese.
2. Manganiferous iron ores with from 10 to 35 per cent of manganese.
3. Ferruginous ores with from 5 to 10 per cent of manganese.

536. Uses. The most important use of manganese is in the steel industry. Small quantities are used to deoxidize and desulphurize the molten metal. Larger quantities make an alloy steel which possesses extraordinary toughness. Small quantities of it are used in nichrome, Monel metal, German silver, and manganese bronze. *Manganin*, a copper alloy containing from 12 to 15 per cent of Mn, is used in resistance coils. Manganese dioxide is used to decolorize glass. A very large tonnage of manganese is used in the manufacture of the familiar dry cell of commerce. Other uses are in the manufacture of driers for paint, and brown and green pigments for the same purpose.

537. Marketing, production, and prices. Pure metallic manganese is not ordinarily produced. The metal appears on the market in the form of ore, ferromanganese, and spiegeleisen. The prices of these products, which vary with conditions in the steel industry more than with anything else, are given in Table LXII.

TABLE LXII. PRICES OF MANGANESE ORE, FERROMANGANESE, AND SPIEGELEISEN (IN DOLLARS PER LONG TON)

YEAR	ORE (50 PER CENT)	FERROMANGANESE (80 PER CENT)	SPIEGELEISEN (20 PER CENT)
1910	13.00	42.45	25.00
1915	15.84	105.83	26.20
1920	33.63	193.21	70.11
1921	14.04	79.53	31.25
1922	15.91	74.22	34.31
1923	33.51	114.85	42.87
1924	30.70	102.85	34.41
1925	32.29	114.79	32.40
1926	30.70	95.02	32.83
1927	30.70	94.50	34.17

The manganese industry in the United States is essentially a "war baby." Before 1914 there was only one producer turning out less than one half of our domestic requirements. This production rose during the World War to 90 per cent of our requirements, but has since fallen off again. The production of other countries is indicated in Table LXIII.

TABLE LXIII. WORLD'S PRODUCTION OF HIGH-GRADE MANGANESE ORE (IN METRIC TONS)*

YEAR	BRAZIL	INDIA	RUSSIA	UNITED STATES
1910	253,953	813,761	668,050	2,294
1915	288,671	457,622	537,362	9,767
1920	453,737	748,296	95,122	95,940
1921	275,694	690,223	28,821	13,747
1922	340,706	482,039	195,753	13,619
1923	235,831	706,245	413,960	32,006
1924	159,229	815,894	499,799	57,422
1925	302,305	852,934	816,507	99,902
1926	311,253	—†	973,000	47,003

* Mineral Industry. † Not available.

Metallurgy

538. General. The preparation of the metal or its compounds depends upon the form in which it is to be marketed. For the purposes of this text it will be discussed under (1) metallic manganese; (2) alloys; (3) manganese dioxide.

539. Metallic manganese. The purest metal can be produced only by the thermite process (reduction of the pure oxide by means of powdered aluminum). By this means it is possible to produce a metal containing about 3 per cent of impurities, chiefly Si, Fe, and Al. It is very difficult to eliminate the last traces of these impurities. Electrolysis from sulphate solution is possible, but the deposited manganese is powdery. In another process the manganese ore containing iron is calcined with coal at a temperature of about 1100° C. The iron thus reduced is removed and the calcine smelted in a blast furnace with coke. This produces, not metallic manganese, but a high-grade ferrous alloy.

540. Alloys. Since a very large percentage of the manganese is used in the manufacture of steel, it is not essential to remove all the carbon and iron. For this reason the commercial form of the metal is usually an alloy (ferromanganese) containing from 70 to 80 per cent of Mn, 6 per cent of C, and the remainder of Fe and Si. Another form of the alloy is spiegeleisen, containing from 15 to 20 per cent of Mn, 5 per cent of C, and the remainder of Fe and Si.

The commercial alloy is produced by the reducing smelting of high-grade manganese dioxide ore. It is more difficult than ordinary smelting, owing to the fact that MnO_2 tends to enter the slag and that Mn is volatile at the temperature used in smelting. For these reasons the loss in smelting is frequently of the order of 15 to 20 per cent. A high temperature and a very strong reducing action are maintained. Under such conditions it is inevitable that the Fe, Si, and C be also reduced, and only by employing the highest-grade ore can ferromanganese of a 75 per cent grade be produced. Ferromanganese with a carbon content of less than 1 per cent can be produced by heating ferromanganese with MnO_2 in an electric furnace to a temperature of 1700° C.

541. Manganese dioxide. Next to the manufacture of steel, that of dry batteries consumes the largest tonnage of manganese.

In these it is used as a depolarizer, and its effectiveness depends to a large extent upon its freedom from metals electronegative to zinc, such as Cu, Ni, Co, and As. It is essential, then, that the manganese dioxide be very pure, and since most ores contain less than 80 per cent MnO_2, some cheap method of purification is necessary — cheap because it must meet keen competition from certain pure Russian ores.

A very pure dioxide can be produced by the Westling process. In this process the crude ore is crushed to pass a 20-mesh screen and digested for several hours in vats with sulphurous acid. This converts most of the manganese into the sulphate. The Fe, Al, and As are precipitated with limestone and the Cu with powdered aluminum, and calcium nitrate is added to form manganese nitrate. The residue is separated out by filtration. The clear solution of manganese nitrate is evaporated in open pans to remove calcium sulphate, and then heated under pressure to decompose the nitrate into MnO_2 and nitric anhydride. The latter is recovered as HNO_3. This purified dioxide finds wide use in the manufacture of other chemicals, pigments, and glass.

In Van Arsdale's process the low-grade ore is crushed to 30 mesh, suspended in water, and exposed to the action of SO_2 gas. The following reactions go on:

$$MnO_2 + SO_2 = MnSO_4.$$
$$MnO_2 + 2\,SO_2 = MnS_2O_6.$$

After a protracted digestion at high temperatures the solution is filtered in order to remove insoluble material, and the clear solution is evaporated. Water and SO_2 are driven off, leaving a residue of $MnSO_4$. This residue is then calcined in a rotary kiln at a temperature of about 1100° C., yielding MnO_2 about 99.5 per cent pure.

CHROMIUM

542. Physical and chemical properties. Chromium is a bluish-white metal having a specific gravity of 6.92. It has a very high melting point (between 1520° and 1530° C.). It is not affected by exposure to the atmosphere and oxidizes slowly at higher temperatures. It dissolves in dilute H_2SO_4 or HCl but not in concentrated HNO_3. It has approximately the hardness of glass.

543. Ores. Nearly all our chromium is derived from one mineral, — chromite ($FeO \cdot Cr_2O_3$). The pure mineral contains 68 per cent of Cr, but the ores range from 35 to 55 per cent Cr_2O_3. The principal sources of supply of this mineral are Rhodesia, New Caledonia, Canada, and the United States, although our domestic resources are very limited.

544. Uses. The two most important uses are as ferrochrome in the steel industry and as a refractory material for lining metallurgical furnaces. Chromium imparts hardness and high tensile strength to steel. Chrome bricks, although high in price, are particularly valuable because they resist well both acid and basic slags and possess a very high softening point. They are often used to separate an acid roof and a basic wall or hearth in a reverberatory furnace.

Chromic salts have an extensive use in the tanning industry, and insoluble chromates are useful as yellow pigments. Stellite, a stainless alloy for cutlery and tools, contains chromium, as does nichrome, an alloy used as resistor material in the construction of electric heaters and furnaces. It is marketed as metallic chromium, ferrochromium, or chromite; so its manufacture can best be discussed under these heads.

545. Production and prices. Since all our chromium is derived from chromite, the production of that mineral is a measure of our capacity. Table LXIV gives the production of chromite during the past few years.

TABLE LXIV. PRINCIPAL PRODUCERS OF CHROME ORE (IN METRIC TONS)

	1917	1918	1919	1920	1921	1922	1923	1924	1925
Canada	32,978	19,953	8,678	9,996	2,538	696	3,228	—	—
Cuba	—	9,000	14,693	721	610	1	10,587	8,276	30,310
Greece	6,750	10,887	9,054	7,382	8,029	9,213	14,828	14,327	—
India	27,497	58,670	37,024	27,232	35,322	23,144	55,115	46,194	—
Japan	8,939	6,247	6,012	3,967	3,368	3,756	4,528	5,376	5,815
New Caledonia	41,892	26,000	23,548	91,536	29,458	10,718	23,226	15,292	—
Rhodesia	74,133	31,789	32,007	54,674	45,533	84,799	87,702	156,692	123,222
United States	44,429	83,753	5,161	2,542	256	361	231	237	110

The price range during recent years is shown in Table LXV. The sharp rise during 1917 and 1918 was due, of course, to war demands in the shape of alloy steels and refractories.

Table LXV. Average Prices of Chromite in the United States

Year	Cents per Long-Ton Unit
1910	30
1915	45
1916	80
1917	100
1918	140
1919	95
1920	78
1921	55
1922	45
1923	44
1924	41
1925	46
1926	45

Metallurgy

546. Metallic chromium. Pure chromic oxide is prepared from sodium bichromate and sulphur thus:

$$Na_2Cr_2O_7 + S = Na_2SO_4 + Cr_2O_3.$$

This material is washed free from all sodium sulphate and then reduced by the thermite process. In this process the powdered Cr_2O_3, together with finely divided metallic aluminum, are placed in a pot lined with magnesite. When the mixture is ignited, the reaction goes on thus,

$$Cr_2O_3 + 2\,Al = 2\,Cr + Al_2O_3,$$

with a considerable evolution of heat, — enough to melt the chromium. With proper precautions this metal will be free from all impurities except Al.

547. Chromates. Much of the chromium used in industry must be in the form of the chromate or bichromate. In the manufacture of this the chrome ore (at least 40 per cent Cr_2O_3) is given an oxidizing roast, to eliminate any sulphur that may be present, and another roast with sodium carbonate and limestone. The following reaction goes on:

$$4\,FeCrO_4 + 4\,Na_2CO_3 + 2\,O = 2\,Fe_2O_3 + 4\,Na_2CrO_4 + 4\,CO_2.$$

The limestone is added in order to prevent sintering and to render the charge more porous. The charge is rabbled at fre-

quent intervals during the roasting period of from eight to sixteen hours. The chromate thus formed is leached out with boiling water and the calcium precipitated with Na_2SO_4. This solution is then decanted and filtered, and pure crystals of Na_2CrO_4 are obtained by evaporation and crystallization. The bichromate can be obtained by treatment with sulphuric acid thus:

$$2\ Na_2CrO_4 + H_2SO_4 = Na_2Cr_2O_7 + H_2O + Na_2SO_4.$$

548. Ferrochromium. Ferrochromium is now produced in the electric furnace by the reduction of chromite by means of coal or coke. Lime, fluorspar, and quartz are added as required in order to produce a slag of the desired chemical composition. The following reactions represent the two extremes of reduction:

$$FeO \cdot Cr_2O_3 + 4\ C = Fe \cdot 2\ Cr + 4\ CO.$$
$$9(FeO \cdot Cr_2O_3) + 50\ C = 2\ [(Fe_3C \cdot 3\ Cr_3C_2)] + 3\ Fe + 36\ CO.$$

The first reaction produces a carbon-free alloy; the second, one containing 10.4 per cent of carbon. In practice the alloy varies from 4 to 8 per cent C, according to the furnace conditions and the character of the ore. Separation of the slag from the metal takes place in a pot outside the furnace. Low-carbon ferrochromium may also be made by the thermite process.

549. Chromium plating. Electroplating with chromium has become very popular in the last few years. Because of its resistance to atmospheric corrosion and its superior hardness, chromium makes an almost ideal wearing surface. Furthermore, electrolytic chromium is malleable, while the ordinary chromium is brittle. The plating is carried out in a chromic acid solution containing a small percentage of chromic sulphate, using lead, platinum, or chromium anodes. The character of the deposit is determined by the strength of the solution and the current density.

NICKEL

550. Physical and chemical properties. Nickel is a silvery-white metal, malleable, ductile, and slightly magnetic. It has a specific gravity of 8.84 and melts at 1450° C. When in the cast condition it has a tensile strength of from 50,000 to 60,000 pounds per square inch, but by heat treatment and mechanical work

this may be brought up to from 120,000 to 140,000 pounds. Its electrical conductivity is about 16 per cent of that of copper. At ordinary temperatures it is not acted upon by air or water. It is attacked with difficulty by HCl and H_2SO_4 but readily by HNO_3. It alloys readily with many metals.

551. Marketing and prices. The form in which nickel is marketed depends upon the purpose for which it is to be used. Concerns using large quantities prefer to buy the metal in the form of ingots about $15 \times 16 \times 3$ inches, weighing about 50 pounds. For smaller users the most convenient form is that of shot or pellets. These are packed in barrels, each barrel holding 500 pounds net. A small amount of electrolytic nickel is marketed directly in the form of cathodes about 2.5 feet square and from $\frac{1}{16}$ inch to $\frac{1}{2}$ inch thick. Sometimes these are cut up into smaller pieces and packed in 50-pound parcels for the convenience of certain customers. Cubes, disks, and rondelles ($1\frac{1}{2}$ inches in diameter and $\frac{3}{4}$ inch thick) are the common forms of the imported metal.

Before the World War one strong company, with mines in Canada, practically controlled the market, and fixed prices. Since then, however, three other concerns, with a total capacity about equal to the one company, have entered the field, so that the price is now fairly well stabilized. The price range during recent years is indicated in Table LXVI.

Table LXVI. Price of Metallic Nickel

Year	Cents per Pound
1910	40.0
1915	40.3
1917	47.5
1920	41.0
1921	38.0
1922	31.6
1923	28.1
1924	28.2
1925	30.9
1926	36.0

552. Production. About 90 per cent of the world's nickel comes from two sources, — Sudbury (Ontario) and New Caledonia. The production in recent years is indicated in Table LXVII.

Table LXVII. World's Production of Nickel (in Metric Tons)

	Sudbury	New Caledonia	World Total
1900	—	6584	8,280
1910	18,636	5237	25,200
1915	34,039	2569	42,000
1919	22,035	2000	26,000
1920	30,615	2400	34,000
1921	9,628	1660	12,000
1922	8,667	2300	11,000
1923	31,028	1700	33,000
1924	34,000	2700	37,000
1925	35,000	2500	38,000
1926	37,000	2600	39,600

553. Ores. Unfortunately the United States has no deposits of nickel ores. We are entirely dependent upon foreign sources for our supplies. As a matter of fact there are but two commercial deposits in the world, — one at Sudbury (Ontario), and the other on the island of New Caledonia, a French possession in the Southern Pacific. At Sudbury the metal occurs as pentlandite ((Ni, Fe)S), along with chalcopyrite and pyrrhotite, the average ore containing about 1.5 per cent of Cu and 4.4 per cent of Ni. At New Caledonia the mineral is garnierite ($(Ni, Mg)SiO_2 \cdot H_2O$), containing about 5 per cent of Ni. Since all the New Caledonia ore is shipped to Europe for reduction, only the details of domestic practice will be discussed in this text.

554. Uses. The principal use of nickel in this country is in the manufacture of alloy steels, about 65 per cent of the production being so used. These steels contain from 1 to as much as 50 per cent of the metal. Nickel possesses the property of conferring great hardness and strength on steel without seriously impairing its ductility. Such steel finds important uses in ordnance, automotive equipment, structural steel, and railroad and power-plant equipment. A great deal of nickel is also used in the electroplating industry. Monel metal (67 per cent Ni, 28 per cent Cu, 5 per cent Fe, Mn, Si, and C) has the properties of steel and the appearance of nickel, and will resist well the action of steam, sea water, hot gases, and acids. Nickel-silver for tableware and jewelry, nickel-chromium alloys for the resistors of heating furnaces, and permalloy, which has extraordinary magnetic permeability, are also important uses of the metal.

Metallurgy

555. Reduction of nickel. The metallurgy of nickel can best be described under (1) roasting the raw ore; (2) smelting to matte; (3) converting; (4) refining (Mond process and top-and-bottom process).

556. Roasting. The raw sulphide ore is roasted in heaps. This antiquated method can be employed only when both labor and ore are cheap and the location of the property is an isolated one. The following process is used at one of the plants at Sudbury, Ontario. In building the heaps an area of ground about 100 feet long and 60 feet wide is covered to a depth of about 3 feet with sticks of cordwood. Coarse and fine ore, in the proper proportions to insure even burning, are then placed on the cordwood to a depth of from 6 to 9 feet. The wood is ignited at several points and the roasting controlled by throwing fine ore on the surface of the heap. The average heap will contain from 4000 to 5000 tons of ore and will require from eight to ten months to reduce the sulphur from 25 per cent to 10 per cent. Since only a limited amount of fine ore can be used in building the heap, the major portion of this must be screened out and sent on to the reverberatory plant for treatment.

557. Smelting. The treatment in this step depends upon the size and condition of the ore. The coarse roasted ore from the heaps is mixed with a small amount of flux (the ore is practically self-fluxing) and 11 per cent of coke and smelted in a 194 × 50 inch water-jacketed blast furnace. Two products are made, — matte and slag, — which are separated from each other in a settler. The composition of these two products, in per cents, is about as follows:

	Cu + Ni	Fe	S	SiO_2	Al_2O_3	CaO	MgO
	Per Cent	*Per Cent*	*Per Cent*	*Per Cent*	*Per Cent*	*Per Cent*	*Per Cent*
Matte . . .	23.00	45.50	26.50	—	—	—	—
Slag	0.48	44.00	2.20	31.00	7.50	3.50	2.50

The fine ore, not suitable for heap roasting or the blast furnace, is sent to the reverberatory plant. Here it is all crushed to about 20 mesh and roasted in Wedge furnaces down to 10 per cent sulphur. This roasted material, with a little raw ore to

bring the sulphur content up to the proper point, is then smelted in 19 × 112 foot reverberatory furnaces. The slag and matte from this operation are of approximately the same grade as from the blast furnaces and are handled in the same way.

558. Converting. The next problem is to eliminate the bulk of the iron from the Cu-Ni-Fe matte. This is accomplished by oxidation and slagging in basic-lined converters, each 10 × 37 feet and holding 100 tons of matte. This matte is brought, in a molten condition, from the reverberatory or blast furnace and blown down with a siliceous flux. A converter campaign will last for about sixty hours, and during that period about 450 tons of matte will be charged. A high-grade matte is thus produced which will average 79 per cent of Cu + Ni and 0.3 per cent of Fe. This is cast into conveniently shaped ingots for shipment to the refinery. The converter slag will contain about 4.5 per cent of Cu + Ni, 46 per cent of Fe, and 2.5 per cent of sulphur. This is sent back to the reverberatory furnace for re-treatment.

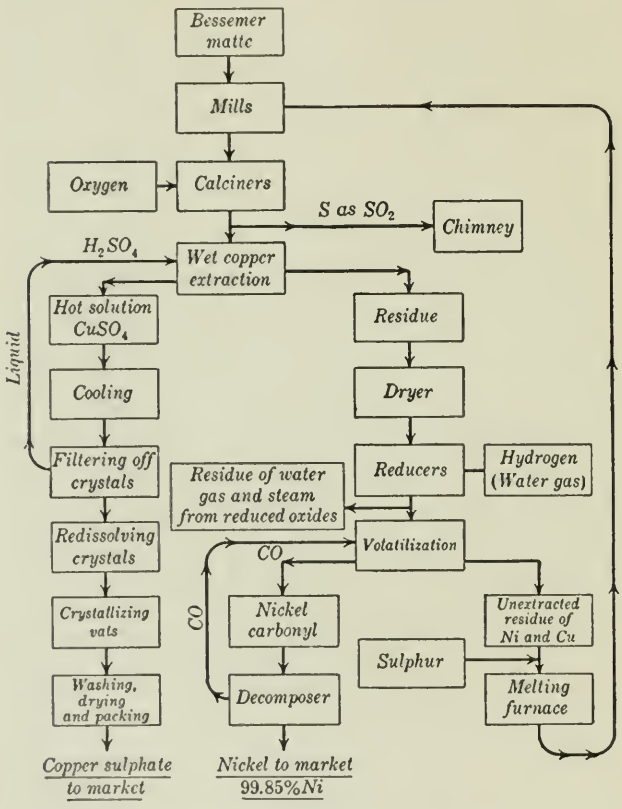

FIG. 158. The Mond process

559. Refining (Mond process). A large part of the Cu-Ni matte produced at Sudbury is shipped to Swansea, Wales, to be refined by the Mond process (see Fig. 158). In it advantage is taken of the fact that nickel forms with CO a volatile compound, nickel carbonyl ($Ni(CO)_4$). Only by this means or by electrolysis can the pure nickel be made. All other nickel contains small amounts of Cu and Fe.

The matte from the Bessemer converters (containing about 40 per cent of Ni and 40 per cent of Cu) is ground to pass a 60-mesh screen and is then roasted in mechanical furnaces in order to eliminate most of the sulphur. This calcine is leached with hot dilute sulphuric acid in order to dissolve the copper as sulphate. Separation and washing of the residue is accomplished by filtering, and the clear liquor is passed on to the crystallizer. Here the pure $CuSO_4$ crystals are made for market, and the mother liquor containing Ni is returned to the system.

The residue from the sulphuric acid treatment is dried and then fed into the reducers. These are mechanical devices similar to Wedge furnaces, in which rotating arms cause the ore, in a thin sheet, to pass from shelf to shelf down through the apparatus. Water gas (mostly hydrogen) is passed up through the reducer, countercurrent to the ore. A temperature of about 300° C. is maintained, and most of the nickel is thus reduced to the metallic state. The material from the reducers is then cooled and passed on to the volatilizers, which are similar devices. Here, at a temperature of about 80° C., it is exposed to the action of CO gas. The gaseous nickel carbonyl formed is then conducted to a vertical cylinder, filled with pure nickel shot, called the decomposer, which is kept at a temperature of about 300° C. At this temperature the reaction reverses itself and the carbonyl decomposes, leaving metallic nickel on the surface of the shot and returning CO gas to the system. Connected with the cylinder is a device for screening out the larger pellets and returning the smaller ones to the cylinder for another load of nickel. This nickel contains as impurities not more than 0.06 per cent of Fe and 0.09 per cent of Cu.

560. Refining (top-and-bottom process). This process, sometimes called the sodium sulphide process, is based upon the fact that when sulphides of Ni, Cu, and Na are fused together, a separation takes place in the formation of two layers. The lower layer contains most of the nickel sulphide; the upper, most of the sodium and copper. The process as now carried out is as follows: The Bessemer matte, containing about 80 per cent of Ni + Cu and 0.3 per cent of Fe, is charged into a blast furnace with either sodium sulphide or crude sodium sulphite and coke. The molten matte is drawn off, cast into slabs, and allowed to cool. A sharp separation takes place with about

90 per cent of the copper in the upper layer. The bottom is then smelted again, after which it will contain about 70 per cent of Ni, 0.9 per cent of Cu, 0.3 per cent of Fe, and a remainder of Na and S. It is then washed with water to remove Na_2S and with H_2SO_4 to remove Fe. The Cu is removed by chloridizing and leaching. The leached material is given an oxidizing roast and then reduced in open-hearth furnaces to metallic nickel. Further refining may be carried on by electrolysis.

561. Hybinette process. The separation of the Ni from the Cu, Fe, and other impurities may be carried out electrolytically by the Hybinette process. The flow sheet of the process is shown in Fig. 159. Deposition is carried out in wooden, lead-lined tanks about 25 feet long, 2.5 feet wide, and 4 feet deep. Each tank contains 35 cathodes and 36 anodes. The former are made of iron plate, while the latter are cast from material averaging 65 per cent Ni, 29 per cent Cu, and 5 per cent S. The electrolyte consists of a slightly acid solution of nickel sulphate. Each cathode is suspended in a wooden frame with canvas sides, a small hydrostatic head being maintained by means of purified electrolyte. This causes a flow of the solution from the cathode to the anode compartment and thus prevents the copper-bearing anolyte from having access to the cathode.

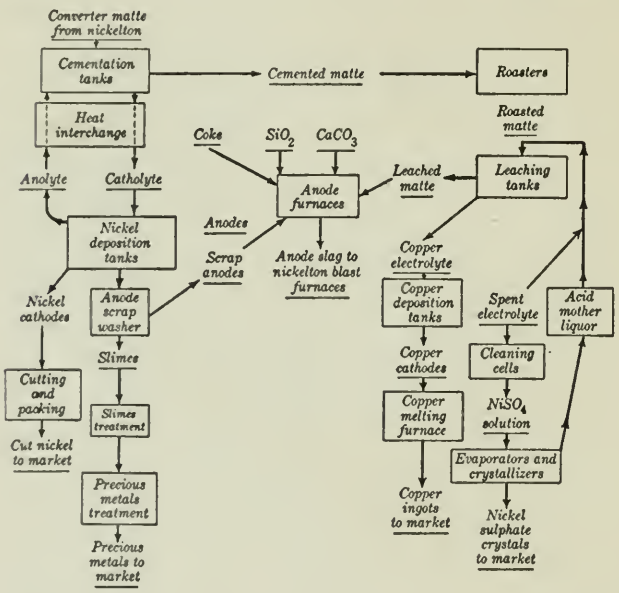

FIG. 159. Flow sheet of the Hybinette process

It will be recalled that the position of nickel in the electrolytic series is as follows: Cu, H, Pb, Ni, Co, Fe. It is evident, then, that although copper is deposited in preference to hydrogen, the opposite is true of nickel. Successful deposition of the nickel is accomplished only by maintaining a far greater concentration of the Ni ions. It is also necessary to have about 0.25 gram per

liter of acid present in order to prevent the deposition of basic salts on the cathode. The current density used is about 8.3 amperes per square foot of cathode surface at a voltage of from 2 to 4 volts.

The foul solution for cementation passes through a preheater, where the temperature is raised to about 85° C. The cementation tanks are filled with granulated matte, and the solution is circulated through it. Metallic copper is deposited, while the nickel, together with about one half of the iron of the matte, goes into solution. The nickel content of the solution is kept fairly high, — about 50 grams per liter. The pure solution then passes through a heat interchange, and finally to the storage tanks for distribution to the cathode frames. Portions of the electrolyte are withdrawn from time to time for purification. The electrolytic nickel analyzes as follows:

	Per Cent
Ni	98.25
Co	0.75
Cu	0.03
Fe	0.50
C	0.10
Pb	0.20

COBALT

562. Physical and chemical properties. Cobalt is a bluish-white metal resembling nickel. It has a specific gravity of 8.79 and melts at 1444° C. The tensile strength varies with heat treatment and mechanical work from 34,000 to 64,000 pounds per square inch. It is magnetic up to 1100° C. It is soluble in most acids.

563. Ores. There are a number of cobalt minerals, among them being cobaltite (CoAsS), smaltite ($CoAs_2$), cobalt bloom ($Co_3As_2O_8 \cdot 8\,H_2O$). Cobalt is also found as an impurity in many nickel and arsenic ores. The most important deposits now known are in Cobalt (Ontario), in New Caledonia, and in the Belgian Congo.

564. Uses. Cobalt is an essential constituent of stellite, a cobalt-chromium alloy used in the place of high-speed steel. Cobalt compounds are used in the paint-and-varnish industry to decrease the time of drying and in the manufacture of glasses and enamels. Considerable research has been conducted

lately on the use of cobalt steels for magnets in electrical industry. There appears to be an unworked field for it in the general steel industry as an alloying agent.

565. Production, marketing, and prices. Cobalt is produced in a small way in many countries. At the present time the metal is being produced in Saxony, Belgian Congo, New Caledonia, Australia, and Ontario. It is almost impossible to obtain any accurate figures concerning production, since more often than not the metal is a by-product in the refining of other ores. The United States produces practically no domestic metal. It is estimated that the domestic consumption (expressed in terms of the pure metal) is in the neighborhood of 1000 tons per year.

Cobalt metal is marketed in the form of rondelles (1 inch in diameter and $\frac{3}{4}$ inch thick), shot, and anodes. These are packed in small casks for shipment. Most of the ceramic cobalt is sold in the form of the oxide, and this too is barreled for shipment.

The price is governed entirely by conditions in the steel and ceramic industries. Up to 1907 the metal sold for about $2.50 per pound, but the discovery of the cobalt-silver ores of Cobalt (Ontario) sent the price down to less than $1 per pound, where it stayed for several years. Cobalt was then a drug on the market. Since then, however, it has come back slowly and in 1927 was quoted at $2.25 per pound.

The high-grade cobalt metal should contain 97 per cent of Co, the impurities consisting of Ni, C, Fe, Cu, Si, and Mn. Ordinarily the specifications call for less than 0.5 per cent of Ni and less than 1 per cent of C. The cobalt oxide is produced in two grades, a 70 per cent grade and a 75 per cent grade. The limit of nickel in both grades is 1 per cent.

Metallurgy

566. General. The preparation of pure metallic cobalt is a complicated process, because of the fact that its ores are of a low grade and that the cobalt occurs in combination with such elements as Ni, Fe, As, and Sb, from which it is separated only with difficulty. The process, for study, can best be divided into the following steps: (1) blast-furnace smelting; (2) roasting

of speiss; (3) sulphatizing and dissolving; (4) elimination of iron and copper; (5) precipitation and reduction of cobalt.

567. Blast-furnace smelting. Most of the domestic metal is obtained from the ores of Cobalt, Ontario, where it occurs with Ag, Fe, and Ni as arsenides and sulphides. The ore is mixed with the proper fluxes to give a fusible slag and smelted with about 12 per cent of coke in a small blast furnace. The products of the blast furnace are crude silver bullion, speiss, matte, and slag. It differs from the ordinary blast-furnace smelting only in that an effort is made, by adjusting furnace conditions, to form as much speiss and as little matte and slag as possible.

The bullion from this smelting will assay from 750 to 800 fine, most of the impurities being Pb and Cu, which may be refined by the usual methods. The speiss will be of about the following composition:

Co	21 per cent
Ni	13 per cent
As	24 per cent
Fe	17 per cent
Cu	3 per cent
Sb	1 per cent
Ag	725 ounces per ton

It is essential that this speiss contain enough As to combine with all the Co and Ni, or these will enter the slag and be lost. The slag will run about 1 per cent Co and Ni combined, and from 3 to 4 ounces of Ag per ton. Frequently, especially when flue dust or rich ores are being treated, it is necessary to return this slag for re-treatment. The matte may be mixed with the speiss and treated as such, or the Co may be thrown away and the matte sold for its nickel and copper alone.

568. Roasting. The speiss from the blast furnace is crushed and ground and then given an oxidizing roast at about 400° C. in order to volatilize the arsenic and antimony. By prolonged roasting the arsenic may be brought down to 4 per cent, but usually it is more economical to stop at about 9 per cent. The gases from these roasters pass through dust chambers and Cottrell apparatus, where much of the arsenic and antimony is condensed. If the silver content warrants it, or no other means are available for the recovery of the silver, the roasted residue may be leached with dilute KCN solution.

569. Sulphatizing. The roasted speiss is next mixed with concentrated H_2SO_4 and thoroughly stirred until the mixture is about the consistency of a thin mud. If the temperature and concentration of the acid are correct, most of the metals are converted into soluble sulphates. This viscous mass is then discharged into dissolving vats, where the water dissolves most of the salts of Co, Ni, Cu, Fe, and As which have been formed. Hydrolysis precipitates most of the Sb. Neutralization of the acid with limestone precipitates the remainder of the Sb and most of the As, Fe, and Ag. This solution is then passed through filter presses, and the cake is washed, dried, and returned to the blast furnace for re-treatment.

570. Elimination of iron and copper. The remainder of the acid is neutralized with $CaCO_3$ in order to precipitate the Fe and As as $FeAsO_4$. The solution is filter-pressed and the cake discarded. To the clear solution Na_2CO_3 is added in order to precipitate the copper as a basic carbonate. Any Co or Ni precipitated may be recovered by crystallization of the $CuSO_4$. Copper may also be removed by electrodeposition or precipitation on iron scrap.

571. Precipitation and reduction of cobalt. The clear solution, now practically free from As, Sb, Fe, and Cu, is treated with sodium hypochlorite. The cobalt is precipitated as $Co_2O_3 \cdot 3\ H_2O$. There should be considerably more Co than Ni in the solution, or the Ni will be precipitated along with the Co. When this begins to occur, which is indicated by the color of the solution, the precipitate is removed before final precipitation of the Co and Ni. This first "mud" (provided pure cobalt is sought) is then washed, dried, and charged, with $CaCO_3$, charcoal, and coke, into an electric furnace. The metal from this reduction (about 99 per cent Co) is "shotted" for shipment.

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CHAPTER XV

IRON AND STEEL

572. General. Iron is easily the master metal. Substitutes have been found for some of our other metals, but nothing can replace iron. It is the very foundation stone upon which is built our life and industry. Unfortunately it is so common that the majority of people are blind to its importance. Without it our bridges, ships, and skyscrapers could not exist; there would be no automobiles or railroads to transport us from place to place, or corn or wheat to nourish ourselves or our animals.

History does not record when or where iron was first discovered. Material evidence of its use by prehistoric peoples is lacking because it is so easily corroded by the atmosphere. Stone, copper, and bronze resist the attacks of water and air, but iron utensils or weapons, even if they were in use four thousand years ago, would long since have succumbed to the ravages of time and disappeared. It has been said that if we were to stop using this metal today, common as it is in our industrial life, one thousand years hence there would not be a particle of the native metal left. All would have been converted into the oxide to mingle with the soil or be dissolved in the water as soluble salts.

It is popularly believed that the Egyptians first used iron in the building of the pyramids, about 4000 B.C. There is excellent evidence that it was used about 1500 B.C. by the Hebrews and Assyrians. In the time of the Cæsars it was a fairly common but by no means cheap metal. This iron was obtained from the ore in a pasty condition and purified and worked by forging. The furnaces then in use could not maintain a temperature sufficiently high to melt the metal. It was not until about A.D. 1350 that the process of obtaining the metal in the liquid state was discovered. Since then the industry has grown rapidly, until today, in those countries fortunate enough to have sufficient supplies of the raw material, the manufacture of iron

and its allied products is easily the most important industry. In the United States this is particularly true, — so much so that the steel industry serves as a veritable barometer of industrial conditions.

573. Physical and chemical properties. Pure iron has a specific gravity of 7.86. It melts at 1530° C. and boils at 2450° C. Annealed iron has a tensile strength of from 36,000 to 41,000 pounds per square inch and a yield point of 16,000 to 21,000 pounds per square inch. All the physical properties of iron are markedly affected by the introduction of other elements, such as C, Mn, S, P, and Si. Pure iron is never used in commerce; its preparation, owing to the ease with which it combines with oxygen, is a laboratory problem. In ordinary iron and steel the impurities are present in amounts ranging from 0.15 per cent in ingot iron or wrought iron to as much as 25 per cent in some special alloy steels.

Chemically, iron is a very active element. It is acted upon by most acids and alkalies and is readily attacked by the oxygen of the atmosphere, especially in the presence of moisture and at temperatures above atmospheric. The corrosion of ferrous alloys is easily one of the most important problems confronting the metallurgist today. One has but to observe the ease with which nails, bolts, and sheet metal corrode, to realize that America's rust bill must amount to tens of millions of dollars annually. The prevention of the rusting or destruction of a ton of iron is far more important than the production of another ton from the ore.

574. Ferrous products.* *Pig iron*, or *cast iron*, is a very impure form of iron made in the blast furnace. It cannot be hardened to any extent by heat treatment, has a low tensile strength, and possesses no elasticity or malleability.

Malleable cast iron is a variety of cast iron in which, by a combined annealing and oxidizing process, a considerable degree of malleability is developed.

Wrought iron is a variety of commercially pure iron which is produced by some process or processes whereby the metal is obtained in a pasty condition and subjected to considerable mechanical work while in that condition.

Steel is a variety of iron which contains sufficient amounts of certain elements, such as C, Mn, Si, P, W, and Cr, to increase

* The Making and Shaping of Steel. Carnegie Steel Company.

markedly its tensile strength, elastic limit, malleability, and ductility. It also possesses the property, which wrought iron, pig iron, and malleable cast iron do not possess, of being hardened when cooled suddenly from certain temperatures.

The development of the metallurgy of iron and steel has brought into common use a large number of special terms used in this industry alone. A few of these terms are defined as an aid to the student:

Cement steel: Made by carburizing bars of wrought iron or soft steel.

Crucible steel: Made by melting, in a crucible, wrought iron, steel scrap, or a mixture of both, with additions necessary to control composition.

Acid Bessemer steel (in this country, Bessemer steel): Made by purifying low-phosphorus (under .090 per cent), molten pig iron with air and making additions, to control composition, to the purified molten metal.

Basic Bessemer steel: Made by purifying high-phosphorus (over 2.00 per cent), molten pig iron with air in the presence of lime, and making additions, to control composition, to the purified molten metal.

Acid open-hearth steel: The raw materials are steel scrap and very low-phosphorus pig iron (under .040 per cent), either cold or molten. These are melted under a flame on a hearth lined with silica sand, the iron oxides formed, together with some ore added, acting as the purifying agent. Additions to control composition of the steel are added to the molten purified metal.

Basic open-hearth steel (in this country, basic steel): The raw materials are iron and steel scrap, iron ore, limestone, and pig iron of medium-phosphorus content, either solid or molten. These are charged on a basic-lined hearth and melted under a flame, the iron oxides and lime acting as purifying agents. Additions to deoxidize and control the composition of the steel are added to the purified molten metal.

Duplex steel: Pig iron of medium-high-phosphorus content is partially purified in an acid Bessemer converter, and then transferred to a basic open hearth, where the purification is completed.

Electric steel: In this country the raw materials are usually steel scrap or molten metal purified by the acid Bessemer or the basic open-hearth process, but pig iron or pig iron and scrap may be used. Heat generated electrically keeps the charge molten while it is being purified with oxidizing and reducing slags and during the additions necessary to control the composition.

Ingot iron: Highly refined steel made in the basic open-hearth furnace, consisting of almost pure iron and containing a maximum of .15 per cent of total impurities.

Simple carbon steels: Steels in which carbon is the only element employed to control physical properties; but they may contain some manganese (less than 1 per cent), with a minimum of other impurities. They may be divided into two main classes:

1. *Hypo-eutectoid steels:* Steels containing less than .85 per cent of carbon. These steels are roughly divided as follows:
   a. *Dead-soft steels:* Made in the basic open hearth and containing less than .10 per cent of carbon and from .20 to .50 per cent of manganese.
   b. *Low-carbon steels:* Containing from .10 to .30 per cent of carbon and less than .60 per cent of manganese. May be made by the Bessemer, the open-hearth, the duplex, or the electric process.
   c. *Medium-carbon steels:* Containing from .30 to .85 per cent of carbon and less than 1.00 per cent of manganese. May be made by any of the processes mentioned under *Low-carbon steels* or by the crucible process.
2. *Hyper-eutectoid, or high-carbon, steels:* Steels containing more than .85 per cent of carbon. These steels seldom contain more than 1.50 per cent of carbon or more than .40 per cent of manganese. They are made by the crucible, open-hearth, and electric processes.

Alloy-treated steels: Carbon steels to which some other element or elements are added to improve their quality, but without markedly changing their characteristics. They are generally of the low-carbon and medium-carbon types and are usually made by the open-hearth, the Bessemer, or the electric process. The elements that may be added for this purpose, in addition to manganese, are small amounts of aluminum, silicon, titanium, copper, phosphorus, sulphur, chromium, molybdenum, vanadium, and tungsten.

Alloy steels: Steels which, in addition to carbon, contain another element or other elements in sufficient amounts to modify the properties to a marked degree over the carbon steel. They may be divided into the following groups:

1. *Simple alloy, or ternary, steels:* Steels that contain only one other alloying element in addition to carbon.
2. *Quaternary steels:* Steels that contain two alloying elements in addition to carbon.
3. *Complex alloy steels:* Steels that contain more than two alloying elements in addition to carbon. These steels are generally high-grade, high-priced steels designed for certain special purposes, and include a great many varieties. The chief representatives, however, are the high-speed steels, which are chrome-tungsten-vanadium, or chrome-tungsten-vanadium-cobalt steels for tools.

575. Steels classified according to use. The working and shaping of iron and steel has developed into a highly specialized industry. The more common iron and steel products, classified according to their use, are defined below:

Structural steel: Used in the fabrication of buildings, bridges, ships, cars, and other structures; mainly low-carbon steels, but includes many varieties of alloy-treated and alloy steels. Made chiefly by the open-hearth process.

Tool steel: Any steel adapted to the manufacture of hand or machine tools. Many varieties, including medium-carbon and high-carbon plain steels and many classes of alloy steels. Made mainly by the crucible and electric processes, but common grades are also made by the open-hearth processes.

Spring steel: Any steel suitable for the manufacture of springs, such as those used on cars, carriages, automobiles, etc. Includes medium-carbon and high-carbon plain steels and quaternary alloy steels. Made by open-hearth and electric processes.

Boiler steel: A high-grade, low-carbon steel especially adapted for use in making boilers. Made by the open-hearth processes.

Rail steel: Any steel suitable for the manufacture of railroad rails. Usually .60 to .85 per cent carbon steel, made by the basic open-hearth process, but some rails are still made by the Bessemer process, in which case the carbon ranges from .30 to .60 in different grades.

Pipe steel, skelp steel, or welding steel: A dead-soft or low-carbon plain steel especially suitable for welding. Made by the Bessemer and open-hearth processes.

Sheet bar and tin bar: Any steel suitable for rolling into sheets. Mainly low-carbon steels made by the basic open-hearth or the Bessemer process, but some is also made by the acid open-hearth process.

Case-hardening steel: Any steel that can be carburized or case-hardened readily. Low-carbon plain steels or ternary or quaternary alloy steels. Made mainly by the basic open-hearth process, but some grades are made by the electric process.

Electrical steel: Usually silicon steels used in the manufacture of electrical machines and apparatus.

Strip steel: Any steel rolled into the form of strips. May be hot finished (hot-rolled strip) or cold finished (cold-rolled strip). Made mainly by the open-hearth process.

Hoop iron: Low-carbon steel in strip form suitable for hoops. Made by the basic open-hearth or the Bessemer process.

Free-cutting steel: High-sulphur steel, for bolts, nuts, screws, etc., that will machine readily. Made by Bessemer or open-hearth processes.

Forging steel: Steel especially suitable for forging, — that is, hammering or pressing. Usually medium-carbon plain steel or quaternary alloy steels. Made by basic open-hearth or electric processes.

Cast steel: A term used in connection with any article of steel formed by casting.

Forged steel: A term applied to articles of steel formed by hammering or pressing.

Wrought steel: A term used in connection with any article of steel formed by forging or hot-rolling, or by hot-working in any way.

576. Economic situation. The United States is the greatest producer of iron and steel in the world. We have enormous reserves of coal, iron ore, and limestone, which are the basic raw materials for the manufacture of iron and steel. The standing of the other countries as well as the growth of the domestic industry is shown in Table LXVIII. The general trend of the price of ferrous products is shown in Table LXIX.

TABLE LXVIII. WORLD'S PRODUCTION OF PIG IRON (IN METRIC TONS)

	United States	Great Britain	Germany	France	Belgium	Russia	Other Countries	Total
1870 .	1,692,378	6,060,720	1,391,123	1,778,113	565,234	359,531	1,012,811	12,859,910
1880 .	3,897,840	7,875,545	2,792,038	1,725,293	608,084	448,596	1,219,832	18,567,228
1890 .	9,353,020	8,033,052	4,658,451	1,962,196	787,836	927,581	1,908,576	27,630,712
1900 .	14,009,870	9,003,046	7,549,655	2,714,298	1,161,180	2,895,636	2,865,207	40,198,892
1910 .	27,636,687	10,380,212	14,794,649	4,032,459	1,803,500	2,740,000	4,472,753	65,860,260
1920 .	37,520,495	8,136,827	5,550,000	3,468,000	1,116,400	98,000	3,980,830	59,870,552
1926 .	39,373,000	2,441,000	9,491,000	9,245,000	3,346,000	2,300,000	11,529,000	77,725,000

ORES OF IRON

577. General. Iron is one of the most common elements in the world, making up, as it does, about 4.5 per cent of the earth's crust. Most of this iron, however, occurs in the form of compounds not readily reduced to metallic iron. There are a very large number of these iron minerals, but few of them are suitable as a source of metallic iron. The silicates of iron are very difficult to reduce; the sulphides render the resulting iron wellnigh useless, while other minerals contain so little iron as to render their use uneconomical. Over 90 per cent of the world's iron is produced today from the various oxides of the metal, and the remainder from the carbonate of iron.

TABLE LXIX. PRICES OF FERROUS PRODUCTS IN THE UNITED STATES *

YEAR	COMPOSITE PRICE OF PIG IRON †	COMPOSITE PRICE OF FINISHED STEEL ‡
1910	$15.08	1.662 cents
1915	13.54	1.534 cents
1917	36.11	4.188 cents
1920	42.76	3.675 cents
1921	22.58	2.532 cents
1922	24.06	2.220 cents
1923	26.30	2.738 cents
1924	20.90	2.609 cents
1925	20.58	2.465 cents
1926	20.42	2.439 cents
1927	18.55	2.357 cents

† Average of basic pig iron at Valley furnace and foundry iron at Chicago, Birmingham, Buffalo, Valley, and Philadelphia. Quoted in dollars per gross ton.

‡ Average of quotations on steel bars, beams, tank plates, plain wire, open-hearth rails, black pipe, and black sheets. Quoted in cents per pound.

578. Hematite. Hematite is the most important iron mineral. It is the sesquioxide of iron (Fe_2O_3), containing 70 per cent of Fe. It is reddish-brown to black in color, and has a specific gravity of from 4.8 to 5.3. It may crystallize, but is more commonly found in the earthy or micaceous form.

579. Magnetite. This is the magnetic oxide of iron (Fe_3O_4), containing 72.4 per cent of Fe. It is black in color, has a metallic luster, and is usually granular and massive.

580. Limonite. Limonite is next in importance to hematite as a source of metallic iron. It is the hydrated sesquioxide of iron ($2\ Fe_2O_3 \cdot 3\ H_2O$), containing 59.8 per cent of Fe. It is dark brown to nearly black in color, has a specific gravity of from 3.6 to 4, and is usually earthy in structure.

581. Siderite. This is the least important of the minerals used as a source of iron. It is the ferrous carbonate ($FeCO_3$), containing 48.2 per cent of Fe. It is light to dark brown in color, has a specific gravity of about 4.7, and usually occurs in cleavable rhombohedrons.

582. Value of an iron ore. Many factors affect the value of an iron ore. Chief among them are its richness, chemical composition, and location. It is obvious that the richer the ore the more attractive it is from the metallurgical point of view, since less

* *The Iron Age.*

flux and fuel are required to smelt it and less time and labor are required to bring it to the desired degree of purity. Richness alone, however, is not the determining factor. The presence or absence of certain other elements affects its value to a great extent. Pyrite (FeS_2), for example, contains 46.6 per cent of Fe, but it is never considered as an ore of iron, owing to the presence of such large amounts of sulphur, — one of the most harmful impurities in steel. Location is an equally important consideration. A 75 per cent ore in northern Canada has no value at the present time, while a 60 per cent ore is worth, let us say, $4.50 per ton at ports on the Great Lakes. In general, ores profitable to smelt will contain from as low as 30 per cent to as high as 65 per cent of Fe, each per cent being termed a unit in describing such ores. Table LXX indicates the range in composition of American ores.

Table LXX. Chemical Composition of Domestic Ores (in Per Cents)

	Fe	P	SiO_2	S	H_2O
Marquette	56.5	0.03	4.6	0.009	11.9
Menominee	55.2	0.06	6.7	—	6.5
Gogebic	56.3	0.03	3.4	—	10.8
Vermilion	61.4	0.04	4.3	—	4.6
Mesabi	56.0	0.03	3.5	—	12.3
Clinton I	37.0	0.30	7.1	0.08	10.1
Clinton II	50.4	0.46	12.1	0.07	3.1
Mineville magnetite	60.9	1.54	4.5	0.02	0.3

583. Bessemer versus non-Bessemer ores. Iron ores are divided into two classes, known as Bessemer and non-Bessemer. The classification is made on the phosphorus content. None of this element is eliminated in the Bessemer process and very little in the blast furnace, so that the phosphorus content of a steel made by a combination of those two processes is governed entirely by the amount of this element in the original ore. Bessemer ores contain less than 0.045 per cent of P; non-Bessemer ores, more than this percentage. The price of Bessemer ores varies from $0.15 to $0.80 per ton more than non-Bessemer ores.

584. Manufacture and purification of pig iron. We come now to the manufacture of iron and steel. No successful process has as yet been devised for the manufacture of steel directly

from the ore. The present process starts with the reduction of the iron from the ore in a blast furnace. One or more processes must intervene before the steel is finished. In this text the processes involved will be studied in the following order: (1) the blast furnace; (2) puddling, or the manufacture of wrought iron; (3) the cementation process; (4) the crucible process; (5) the acid Bessemer process; (6) the basic Bessemer process; (7) the basic open-hearth process; (8) the acid open-hearth process; (9) the electric furnace.

THE BLAST FURNACE

585. General. The oxides of iron are relatively easy to reduce by any of the common reducing agents such as carbon or carbon monoxide. The best appliance yet devised for carrying out this reduction cheaply and on a large scale is the iron blast furnace. The process consists essentially of feeding a mixture of iron ore, coke, and flux into a tall, cylindrical furnace lined with some refractory material. Air at a temperature of about 540° C. is blown in at the bottom of the furnace, maintaining a temperature at this point well above the melting point of the iron. The carbon in the furnace, with the CO produced by the incomplete combustion of this carbon, reduces the iron oxides to metallic iron, which melts and is collected in the crucible of the furnace. Most of the impurities combine with the flux to form an easily melted slag which floats on top of the iron in the crucible. The slag and iron are drawn off from time to time as required.

586. The blast furnace. A modern blast furnace is shown in Figs. 160, 161, and 162. It is a cylindrical furnace, from 80 to 100 feet in height and from 10 to 21 feet in diameter at the tuyères. Because of the fact that it is exposed to a high temperature it must be lined throughout with fire brick, and means must be taken to cool the more exposed parts with water. It can best be studied by describing the individual parts and their uses.

587. Hearth, or crucible, and foundation. The hearth, or crucible, is that portion of the furnace where the molten iron and slag are collected. The diameter of the crucible varies from 10 to 21 feet and the depth from 8 to 11 feet, depending upon

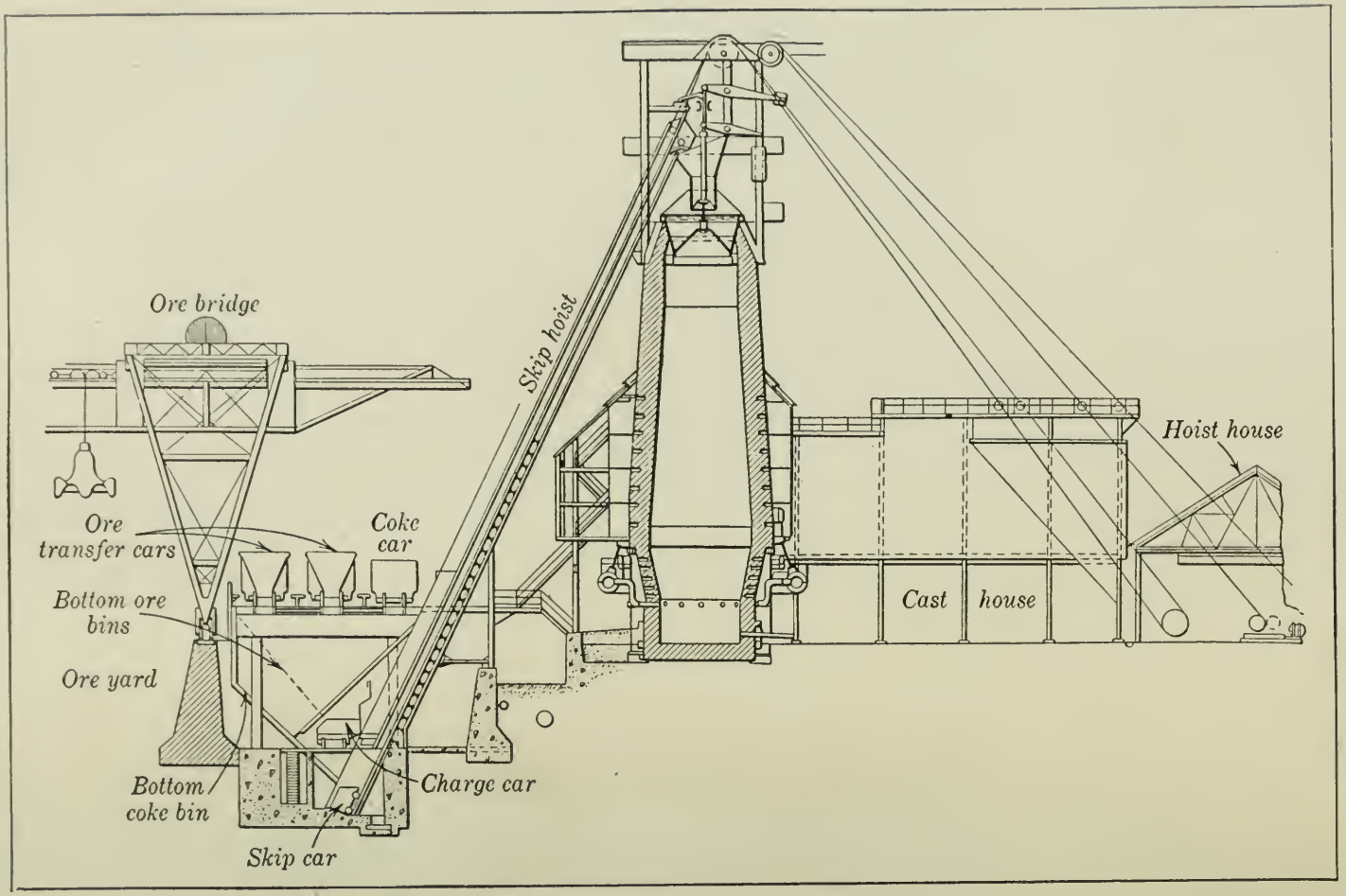

FIG. 160. Section through furnace and stock house

the capacity of the furnace. The walls are built of fire brick and are from 3 to 5 feet in thickness. They must be kept cool by means of water-cooled plates in order to prevent excessive corrosion by the molten slag or metal. The walls are further strengthened by a heavy jacket of steel plates or castings, which in turn are cooled by circulating water. The bottom of the crucible is also built of fire brick, from 6 to 12 feet in thickness. Since the weight of the furnace and charge is tremendous,

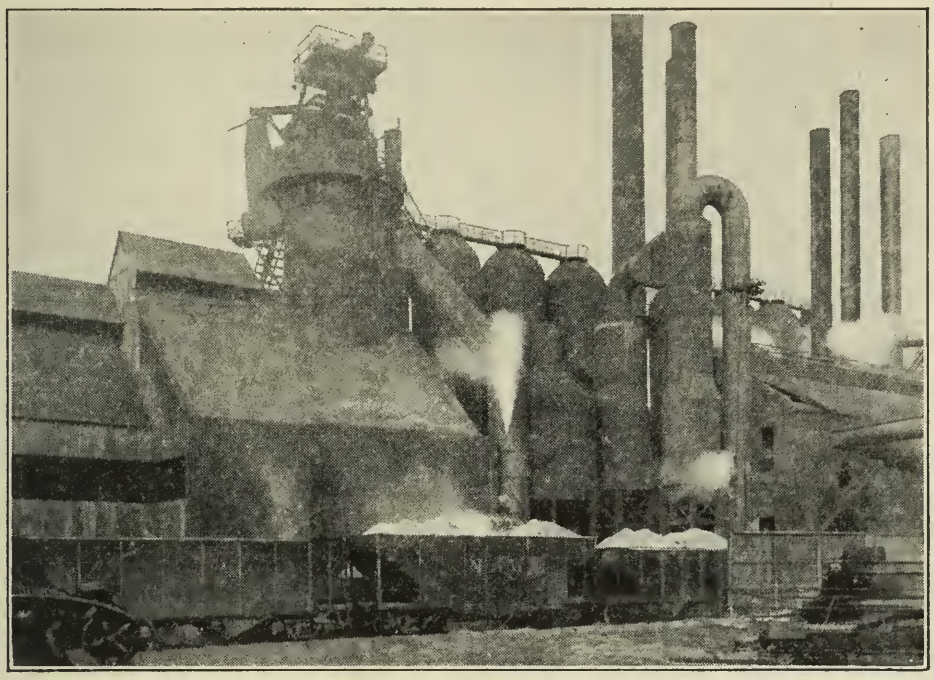

FIG. 161. Blast-furnace plant

Courtesy of the American Rolling Mill Company

it follows that great care must be exercised in placing the foundations, in order to avoid settlement. Any such movement during operation might crack the crucible or mantle walls and cause leaks in the cooling system or damage to the hoisting and charging apparatus.

588. Bosh and mantle. The bosh is that part of the furnace, just above the crucible, where the greatest diameter is attained. It is constructed of fire brick, and since it is not exposed to the heavy pressure of liquid slag and metal, it is not reënforced with a metal jacket. Bosh plates of metal through which water is circulated must be provided at frequent intervals in order to keep the bosh cool and reduce corrosion. The thickness of the

bosh walls is about 30 inches in the larger furnaces. The mantle is a heavy structure of steel which encircles the furnace at the upper limit of the bosh and carries the weight of the shaft and the superstructure. It is in turn supported by columns resting on the foundation of the furnace.

589. Shaft, or stack. The shaft, or stack, is that part of the furnace extending from the upper limits of the bosh to the top of the furnace. As indicated in Fig. 160, it is built with a slight taper to prevent the charge from sticking in its passage through the furnace. The shaft is further divided, arbitrarily, into upper, lower, and middle inwalls. The limits of these three divisions vary somewhat in different districts. The thickness of the fire-brick inwall also varies between wide limits, according to the type of the furnace. In the thick-wall type the inwalls are about 5 feet thick and are seldom water cooled. In the intermediate-wall type the walls are about 3 feet thick, and the lower portions are sometimes protected with cooling plates. In the thin-wall type the walls are from 9 to 18 inches thick, and the entire shell is cooled by plates or with a water curtain. A water trough encircles the furnace just below the upper limits of the bosh in order to conduct away this cooling water, which might otherwise interfere with operations on the casting floor.

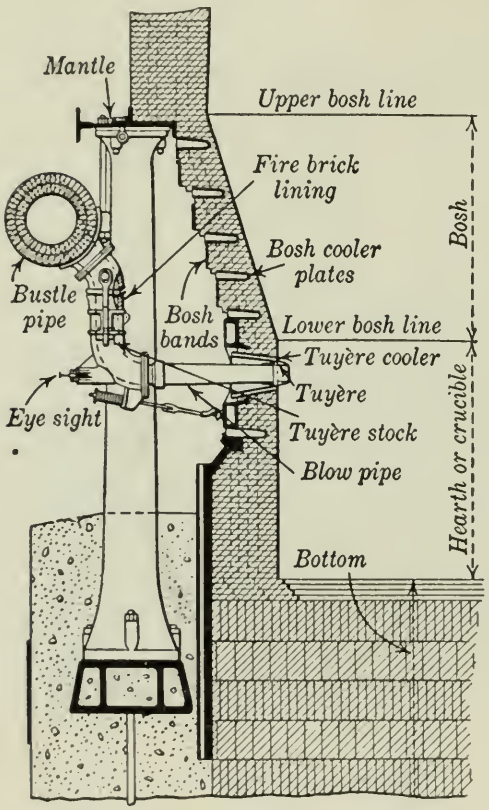

FIG. 162. Blast-furnace hearth and bosh

590. Tapping hole and cinder notch. The tapping hole, or iron notch, for the tapping of the molten iron, is located from 18 to 24 inches above the bottom of the hearth. It is usually a square opening about 8 × 8 inches and may be protected by means of a water-cooled plate.

The cinder notch for the tapping of the slag is located about 2 feet below the tuyère level and from 45 to 90 degrees from the tapping hole. This height, in the modern furnace, allows the accumulation of from 60 to 100 tons of pig iron before there is any danger of drawing some of the iron into the slag when the latter is tapped. The molten slag has a corrosive action on the brickwork, so that it is necessary to use cooling devices. These, termed cinder-coolers, are copper castings through which water is circulated.

591. Tuyères and connections. Air, preheated to about 540° C., and under a pressure of about 15 pounds per square inch, is supplied to the blast furnace by means of the tuyères. These are copper pipes from 4 to 7 inches in internal diameter. There are from ten to sixteen of these, spaced symmetrically about the circumference of the hearth just below the boshes. They determine the height to which slag may rise in the furnace before it becomes necessary to tap. They are exposed for long periods of time to the high temperature maintained at the focus of the furnace, so that it is necessary to cool them with water.

Encircling the furnace, just below the mantle, is the bustle pipe, which supplies the hot blast to the tuyères. This is a steel pipe, about 4 feet in diameter, lined with fire brick. Connection between the bustle pipe and the tuyères is made by means of a blowpipe and tuyère stock. In the tuyère stock, at the curve, is a small opening, called a tuyère cap or wicket, for cleaning the tuyère and for observing conditions in the furnace. By means of a ball-and-socket device it is sealed gas-tight when not in use.

592. Charging devices. The gas given off at the top of the furnace has, under normal conditions, a calorific value of about 95 B.T.U. per cubic foot. In the old days the top was left open to the atmosphere, and this gas was allowed to burn, but today it is the source of most of the power about a steel plant and must be carefully collected and cleaned. It is impossible to charge the furnace without some small waste of gas, but by means of the bell-and-hopper device shown in Fig. 160 this loss can be kept to a very small figure.

There are two circular openings in the top of the furnace. Both of these are sealed by means of a bell, shaped like the inverted frustum of a cone. The upper bell and hopper are considerably smaller than the lower. The various charges of

ore, coke, and flux are hoisted to the top of the furnace and dropped into the upper hopper, the upper bell lowered, and the charge dropped into the lower hopper, which has meanwhile remained closed. When the furnace foreman desires to drop the charge into the furnace, the upper bell is closed and the lower one opened. By this means, at each charging, only the gas caught between the two hoppers is lost. The bells are operated by means of steam, air, or electricity. Devices, varying in different localities, are employed for insuring an even distribution of the charge about the periphery of the furnace. Unless some care is taken to effect this even distribution, the larger lumps of the charge will tend to collect around the edge, to one side or the other. Such inequalities in the texture and composition of the charge will cause channeling in the furnace. These in turn form dead spots in parts of the furnace or such high temperatures in the free parts as to erode the stack walls.

Hand charging of blast furnaces has been entirely superseded in this country by mechanical charging. An inclined railway connects the various bins with the top of the furnace. Formerly a bucket was used to convey the materials along this to the top, but at modern plants the skip, an open-ended car, is used. This is filled and dumped automatically. Often a further economy is effected by using two skips, the empty one aiding in raising the loaded one.

593. Top openings. The gas and dust from the furnace are taken away by means of large openings in the side of the furnace top just below the large bell. These are called offtakes. There are from two to four of these openings, each about 4 feet in diameter. They are connected, by means of fire-brick-lined pipes, with a central large pipe called a downcomer or downtake. On the downtake there are suitable valves and connections for conducting the gas to the stoves, cleaning plant, or power plant, as conditions demand.

Openings, called explosion doors, are provided in the top of the furnace or in the offtakes, to guard against explosions or slips in the furnace. These are designed to open at a certain pressure and thus avoid damaging the furnace structure and endangering the life of the operators. Often vertical pipes called *bleeders* are provided in the offtakes, to allow the escape of any surplus gas. All these pipes and devices must be lined

with fire brick, for they handle gas at an elevated temperature. There is a small opening in the top of the furnace called a try hole. Through this a rod may be inserted to determine the height of the charge in the furnace. In modern furnaces this is often done automatically and recorded in the foreman's office.

Blast-Furnace Stoves and Accessories

594. Stoves. In the early days of blast-furnace operation it was the practice to use air at atmospheric temperature. It was found, however, that preheating the air resulted in great saving.

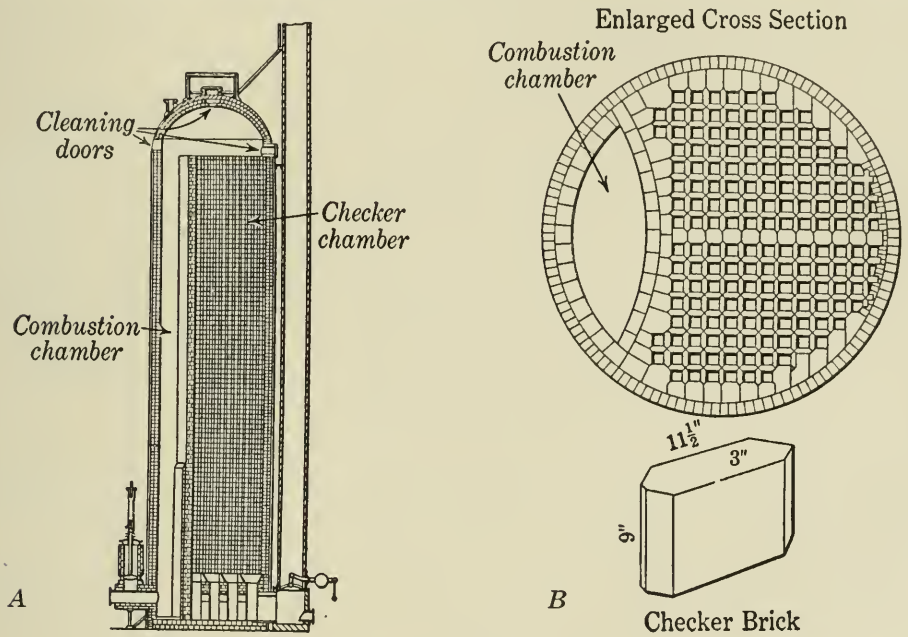

Fig. 163. Foote stove

A furnace of a given size, with preheated blast, is able to treat a much greater tonnage, and the operation is much more even. Today it is the universal practice to preheat all the air used in a blast furnace by means of what are termed stoves. Usually four or five stoves are provided for each furnace or stack. They consist of steel cylinders about 22 feet in diameter and 100 feet in height. They are lined with fire brick and filled with a checker-work of bricks. These bricks are specially shaped so as to present a maximum surface to the gases and heat them up, or in turn be heated, in the least possible time. Such a stove is shown in section, in Fig. 163. This is a two-pass stove, so called because

the gas rises through the combustion chamber and descends through the checkerwork. Three-pass and four-pass stoves, designed to conserve a larger percentage of the heat, are also used. These naturally cost more and take up more plant space. The top of the stove is dome-shaped and is provided with a number of clean-out doors for removing the accumulated dust.

There is an opening at the base of the combustion chamber through which the blowpipe for heating the stove may be inserted. This is so mounted that when the time comes for the stove to be put on air, the burner can be moved back, the door closed, and the cold-blast valve opened. Other valves are provided for controlling the cycle of heating the air. A by-pass is provided for controlling the temperature of the blast, for this must be kept constant if efficient and continuous operation is desired. It is obvious that as cold air is blown through the stove the temperature of the latter changes rapidly. When the temperature of the blast rises too high, the by-pass valve is opened and cold blast is allowed to enter. This valve is gradually closed until, just before the stoves are changed, all the air is passing through the stove. Under ordinary conditions the temperature of the blast is maintained at about 540° C. To heat the air to this temperature requires about 25 to 30 per cent of the total gas produced by the blast furnace. The remainder of the gas is sent to the cleaning plant and used to operate the blowing engines or to generate electricity for sale.

595. Cleaning plant. A flow sheet of a typical gas-cleaning plant is shown in Fig. 164. The gas from the downcomer passes to the dust-catcher, which is simply an enlargement of that part of the flue. It is sometimes 20 feet in diameter, so that the velocity of the gas is checked, its temperature is lowered through radiation, and the larger particles of ore, flux, and fuel carried over by the gas current are deposited on the bottom and sides of the chamber. If this precaution were not taken, this dust would be deposited in the checkerwork of the stoves and insulate these so as markedly to lower their efficiency. Even with considerable care it is necessary to shut down the stoves periodically for clean-outs. In ordinary operation as much as 150 pounds of dust is collected in the dust-catchers for each ton of iron produced. At large plants this dust is sintered and returned to the blast furnace for treatment.

The partially cleaned gas is then passed on to the scrubbers. At a few plants all the gas is treated in the scrubbers, but at most plants the preliminary treatment in a dust-catcher is sufficient for that portion which is to be used in the stoves. For use in internal-combustion engines the last trace of solid matter must be removed, or the cylinders and pistons will be rapidly worn away by abrasion.

The scrubbers consist of vertical cylinders about 12 feet in diameter and 75 feet in height. The gas from the dust-catchers is admitted at the base and the water at the top of these cylinders. Spraying devices bring about an intimate mixing of the air and water and effect an almost complete removal of the

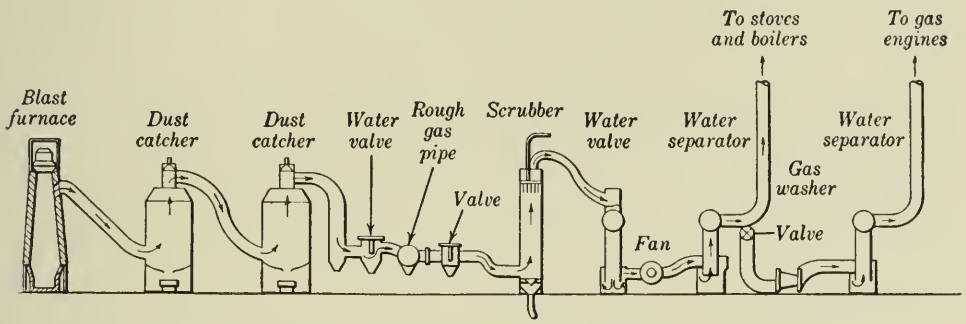

FIG. 164. Gas-cleaning plant

solid matter. The water is conducted away to a settling plant, where the clear water, after cooling, is recovered for further use and the sludge collected. To scrub the gas from the modern blast-furnace plant requires an enormous amount of water, — in large plants as much as 6,000,000 gallons per twenty-four hours being used for this purpose.

The gas enters the scrubbers at a temperature of from 150° to 320° C. and carries about 3.5 grains of dust per cubic foot. It leaves the scrubbers at about 20° C. and carries about 0.2 grain per cubic foot. The gas in the scrubbers is kept under a pressure of from 8 to 16 inches of water by means of fans, in order to insure positive circulation. At some plants water is introduced into the fan in order further to clean the gas. In order to free the cleaned gas from suspended water, it is then passed on to the water-separators, which are vertical, concentric steel cylinders. The outer cylinder is larger in diameter and somewhat longer than the inner one. The gas enters the

top of the outer cylinder and escapes at the bottom through the inner pipe. Entering at a tangent, it is given a spiral motion, and most of the water is deposited on the walls of the separator. The plant illustrated is a rather elaborate one, having a primary and secondary section for rough and final cleaning respectively.

596. Dry blast. In recent years considerable attention has been given to the problem of drying the air used in the furnace. About 60 per cent by weight of the material entering a blast furnace is air. In a 600-ton stack this means about 40,000 cubic feet of air per minute, which will carry with it from 150 to 300 gallons of water per twenty-four hours. This water, at the high temperatures maintained at the tuyères of the furnace, is dissociated, — a reaction which consumes a large amount of energy. In order to conserve this energy, means are provided, at a few plants, for drying this air, either by refrigeration or by desiccation, and thus removing practically the last trace of moisture. Drying tends to produce more even operation by removing another variable, — the moisture content of the atmosphere.

Chemistry of the Blast Furnace

597. Reduction of oxides. Assuming that the furnace is in normal operation with preheated air and that it is being charged in the regular manner, the air will enter the tuyères and, in contact with white-hot coke, will react thus:

$$C + O_2 = CO_2 + 97{,}200 \text{ calories.}$$

Since there is a large excess of carbon at this point, the CO_2 is immediately reduced to CO, thus:

$$CO_2 + C = 2\,CO - 68{,}040 \text{ calories.}$$

This CO, together with the carbon of the charge, then acts upon the iron ore in the descending charge. Any of the following reactions may take place, depending upon the temperature (from 250° to 700° C.) and the furnace conditions (the Fe_2O_3 is probably successively reduced to Fe_3O_4, FeO, and Fe):

$$Fe_2O_3 + 3\,CO = 2\,Fe + 3\,CO_2 + 8520 \text{ calories.}$$
$$2\,Fe_2O_3 + 8\,CO = 7\,CO_2 + 4\,Fe + C + 55{,}920 \text{ calories.}$$

$$3\ Fe_2O_3 + C = 2\ Fe_3O_4 + CO - 16{,}040 \text{ calories.}$$
$$Fe_3O_4 + C = 3\ FeO + CO - 44{,}540 \text{ calories.}$$
$$FeO + C = Fe + CO - 36{,}540 \text{ calories.}$$
$$Fe_2O_3 + 3\ C = 2\ Fe + 3\ CO - 108{,}120 \text{ calories.}$$

The CO_2 formed by the combustion of the carbon, together with that formed in the dissociation of the limestone, tends to prevent the reduction of iron, thus:

$$Fe + CO_2 = FeO + CO - 2340 \text{ calories.}$$
$$3\ Fe + 4\ CO_2 = Fe_3O_4 + 4\ CO - 1360 \text{ calories.}$$

The net result, following the law of mass action, depends upon the relative proportion of CO, C, and CO_2 in the furnace. If there is twice as much CO as CO_2, by volume, the gases will be reducing in action. Ordinarily the gases from a blast furnace contain about 13 per cent of CO_2 and 26 per cent of CO.

The iron, thus reduced in the upper part of the furnace, begins to melt a short distance above the tuyères (from 1400° to 1550° C.) and drops into the crucible. It has meanwhile absorbed considerable amounts of impurities such as Mn, C, S, and P, the kind and quantity of these depending largely upon furnace conditions and the character of the ore.

598. Slag-forming. Any carbonates present in the ore, together with the limestone flux, are dissociated at a temperature of about 1000° C., thus:

$$CaCO_3 = CaO + CO_2.$$
$$MgCO_3 = MgO + CO_2.$$

These oxides then unite with the free silica of the ore to form a fusible slag, thus:

$$CaO + SiO_2 = CaO \cdot SiO_2.$$
$$MgO + SiO_2 = MgO \cdot SiO_2.$$

The various oxides and silicates of Mg, Ca, Al, Mn, etc. present in the ore are dissolved in this slag. The amount of flux added determines the silicate degree of this slag, and this in turn, to a certain extent, governs the character of the iron produced.

599. Impurities. The chief impurities are present in the ore as MnO, Mn_3O_4, SiO_2, P_2O_5, and FeS_2. At the high temperature

maintained at the tuyères a variable proportion of these are reduced by the carbon of the charge, thus:

$$Mn_3O_4 + C = 3\ MnO + CO.$$
$$MnO + C = Mn + CO.$$
$$SiO_2 + 2\ C = Si + 2\ CO.$$
$$P_2O_5 + 5\ C = 2\ P + 5\ CO.$$
$$H_2O + C = CO + H_2.$$
$$FeS + CaO + C = CaS + Fe + CO.$$

From 50 to 75 per cent of the Mn in the ore is reduced and enters the pig iron. High temperatures and basic slags tend to favor this reduction. Manganese also tends to unite with the S of the iron, and the MnS thus formed is dissolved in the slag. Manganese in pig iron varies from 0.25 to 2.5 per cent.

The phosphorus reduced in the furnace forms a phosphide with the iron, Fe_3P, and enters the iron as such. Practically all the phosphorus in the ore is found in the reduced iron. The phosphorus content of pig iron varies from 0.05 to 3 per cent.

High temperatures and acid slags favor the reduction of silicon. It reacts with iron to form a silicide (FeSi), and enters the iron as such. Under normal conditions 90 per cent of the silicon in the ore enters the slag. The silicon content of pig iron varies from 0.5 to 3 per cent.

The elimination of sulphur is likewise incomplete, a variable amount entering the iron as FeS. High temperatures, the presence of Mn, and basic slags favor the elimination of this sulphur. The sulphur content of pig iron varies from 0.03 to 0.1 per cent.

Operation of the Blast Furnace

For the sake of brevity the operations of drying, filling, lighting, and blowing-in the furnace will be omitted. We will assume that the furnace is in normal operation.

600. Charging. The amounts of ore and limestone charged per ton of fuel are referred to as the "burden," and the regulation of these quantities, as "burdening." The calculation of the amounts of flux and ore necessary is too involved for this text. Suffice it to say that from the analyses of the raw materials (see Table LXXI) entering the furnace a balance sheet is drawn up

and the ores apportioned and fluxes added so as to yield a slag of the required silicate degree.

TABLE LXXI. ANALYSIS OF RAW MATERIALS USED IN THE BLAST FURNACE (IN PER CENTS)

ELEMENTS AND RADICALS (DRY BASIS)	FORMULA	ORES				LIME-STONE	COKE
		No. 1	No. 2	No. 3	No. 4		
Silica	SiO_2	6.48	9.04	12.78	5.86	3.43	4.40
Iron	Fe	56.80	54.84	52.93	55.59	.30	1.35
Manganese	Mn	1.14	1.09	.83	.16	.08	.07
Phosphorus	P	.082	.096	.083	.618	.006	.030
Alumina	Al_2O_3	3.22	2.70	3.34	3.63	.86	2.80
Lime	CaO	.11	.18	.25	1.22	51.45	.25
Magnesia	MgO	.14	.26	.21	.87	1.66	.15
Fixed carbon	C	—	—	—	—	—	90.00
Carbon dioxide	CO_2	—	—	—	—	41.43	—
Sulphur	S	—	—	—	—	—	.940
Sulphuric anhydride	SO_3	.03	.04	.04	.06	.060	—*
Alkalies	Na_2O–K_2O	Trace	Trace	Trace	Trace	Trace	Trace
Titania	TiO_2	.018	.009	.012	.019	Trace	Trace
Water (wet basis)	H_2O	14.06	14.50	15.00	12.10	.50	1.50

* Undetermined.

Since the furnace, in normal operation, tends to empty itself rapidly, the charging of the raw materials must be done continually and with great care. The charging is done in "rounds," and all the materials, as determined by the calculations, are carefully weighed in a hopper car. At some plants charging is done by volume instead of by weight. The basis of charging is the weight of fuel in each round. This remains a fixed quantity. The weight of the unit of fuel varies at different plants, from 10,000 to 15,000 pounds being a common range. The order and manner of charging will also vary, according to the physical character of the materials and the condition of the furnace. The cycle employed at one large plant is given below:

One skip of ore, mixture of ores A and B. Weighed. Small bell lowered.
One skip of stone and ore, mixture of stone and ore C. Weighed. Small bell lowered.
One skip of coke, not weighed. Small bell lowered.
One skip of coke. Small bell lowered.
Big bell lowered.
One skip of stone and ore, mixture of stone and ore C. Weighed. Small bell lowered.
One skip of ore, mixture of ores A, B, and C. Weighed. Small bell lowered.

One skip of coke, not weighed. Small bell lowered.
One skip of coke, not weighed. Small bell lowered.
Big bell lowered.

601. Tapping. The slag is tapped from the cinder notch whenever it rises close to the mouths of the tuyères, — in normal operation about every two hours. The slag which has congealed in the cooler is broken through, and the molten slag is allowed to run out into a slag pot or into the granulating launder.

The iron is tapped from the furnace every four to six hours, according to the rate at which it is being reduced and the requirements of the plant. By means of a long auger or drill the clay plug closing the tapping hole is drilled through, and the congealed iron is pierced with a pointed bar or burned out with oxygen if it is of considerable thickness. The molten iron flows out into a ladle or, if pigs are being cast, diverted to the casting bed. A skimmer is provided in the runner, near the furnace end, to divert the slag and stop the last iron and slag. When the crucible is drained and gases pour forth from the tapping hole, the blast pressure is momentarily reduced, a plug of clay is driven into the tapping hole with the clay gun, and the furnace is returned to blast.

TABLE LXXII. THE METALLIC PRODUCTS OF THE BLAST FURNACE (IN PER CENTS)

	SILICON	SULPHUR	PHOSPHORUS	MANGANESE	TOTAL CARBON
No. 1 Foundry .	2.5–3.0	Under .036	.25–1.00	Under 1.00	3.50–4.25
No. 2 Foundry .	2.0–2.5	Under .045	.25–1.00	Under 1.00	3.50–4.25
No. 3 Foundry .	1.5–2.0	Under .060	.25–1.00	Under 1.00	3.50–4.25
Malleable casting	1.00–1.50	Under .050	.2	Under 1.00	3.50–4.25
Forge	About 1.50	Under .100	1.0	Under 1.00	3.50–4.25
Acid Bessemer .	1.00–1.50	Under .050	0.1 or less	About .50	3.50–4.25
Basic Bessemer .	Under 1.00	Under .050	2.00–3.00	Under .50	3.50–4.25
Low-phosphorus acid iron . . .	Under 2.00	Under .030	.030	Under 1.00	3.50–4.25
Basic	Under 1.25	Under .050	.100–1.00	1.00–2.50	3.50–4.25
Spiegel	About 1.00	Under .050	.150	18.0–22.0	5.00–6.00
Ferromanganese .	.50–1.00	Under .030	.10–.30	78.0–82.0	5.00–7.00
Ferrosilicon . .	8.0–15.00	Under .070	.10–.50	—	1.00–2.00
Silico-spiegel . .	8.0–15.00	Under .010	.15	15.00–20.00	—

602. Sampling. The sampling of the iron is very important, for on this depends the price of the iron if it is to be sold

in the open market, or the subsequent purification treatment if it is to be made into steel. Since the chemical analyses require considerable time and the furnace operator must have the information immediately, he is guided largely, in the regulation of his furnace, by sand or chill tests. These are samples cast in small molds about 2 inches in cross section and 4 inches long. From the appearance of the fresh fracture of one of these an experienced operator can judge closely the character of the iron being produced. The samples are taken several times during tapping from the main runner or launder. Similar bars, or sometimes granules, are sent to the chemical laboratory for analysis in order to check up the fracture specimens. Table LXXII indicates the chemical composition of the different products of the blast furnace. Table LXXIII indicates the variation in slags working with different ores and producing different kinds of iron.

TABLE LXXIII. COMPOSITION OF BLAST-FURNACE SLAGS

IRON PRODUCED		SLAG						REMARKS
Si	S	SiO_2	Al_2O_3	CaO	MgO	FeO	S	
Per Cent	*Per Cent*	*Per Cent*	*Per Cent*	*Per Cent*	*Per Cent*	*Per Cent*	*Per Cent*	
3.79	Tr.	33.21	13.67	40.68	11.08	—	—	Cuban ore, hot furnace
0.88	0.07	33.15	10.27	45.57	9.81	—	—	Cuban ore, cool furnace
2.46	0.03	34.84	11.75	41.30	9.79	—	—	Spanish ore, hot furnace
0.35	0.03	30.73	11.32	47.36	8.35	—	—	Spanish ore, cool furnace
1.79	0.03	35.55	12.05	40.52	8.86	0.68	1.66	Lake ore, hot furnace
1.61	0.04	35.35	14.43	29.69	20.71	—	—	Lake ore, cool furnace

PUDDLING, OR THE MANUFACTURE OF WROUGHT IRON

603. General. Pig iron direct from the blast furnace is usually not suitable for use in industry. In castings which require mass alone or for certain kinds of pipe it may be used, but for the manufacture of most articles it must be further purified before it has the requisite physical properties. Wrought iron, the next step in the purification of pig iron, may be defined as a variety of commercially pure iron which is produced by some process or processes whereby the metal is obtained in a pasty condition. It differs from steel in that the latter is in a molten condition during the whole of the purification period. It was

probably the first variety of pure iron to be produced, since it can be made directly from the purer ores.

Wrought iron has a fibrous structure. An ordinary fracture shows this fibrous structure to a degree, but a photomicrograph brings it out much better. Figs. 165, 166, and 167 show a transverse and longitudinal section of a piece of wrought iron containing 0.21 per cent of C. This shows that wrought iron consists of crystals of ferrite (nearly pure iron) with numerous stringers of slag interspersed between these crystals. The orientation of the slag stringers indicates the direction of rolling during the reduction of the piece from the ball. Wrought iron is made from a variety of pig iron termed forge iron, a typical analysis of which is given below:

C	Mn	P	S	Si
Per Cent	*Per Cent*	*Per Cent*	*Per Cent*	*Per Cent*
3.72	0.70	0.36	0.03	1.0

Briefly, the process of puddling consists of purifying the iron while it is in a pasty condition in the furnace. This purification is usually accomplished by a combination of oxidation and mechanical work, — the former to flux the impurities, the latter to eject most of the entrained slag.

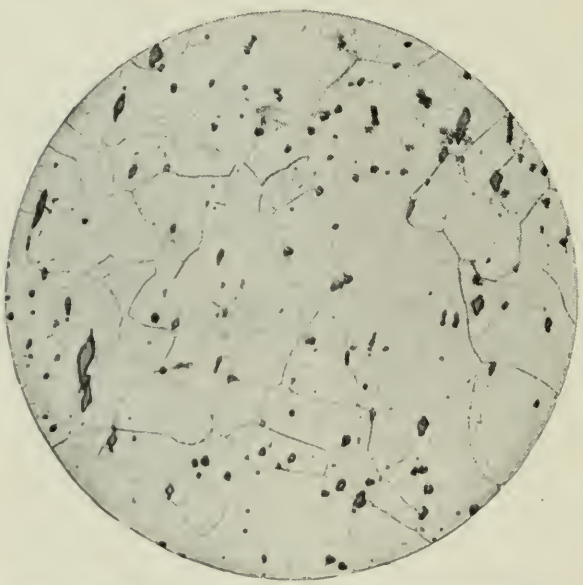

FIG. 165. Wrought iron. (Transverse section) (× 100)

Photograph by Dr. V. O. Homerberg

604. Hand-puddling furnace. Fig. 168 on page 444 shows a typical hand-puddling furnace having a capacity of 500 pounds per heat. Since they are operated by hand labor alone, these furnaces must necessarily be confined to rather small sizes.

The puddling furnace is a special type of reverberatory furnace having a low ratio of hearth to fire box in order that a

FIG. 166. Wrought iron. (Longitudinal section) (× 100)
Nitol etch. (Photograph by Dr. V. O. Homerberg)

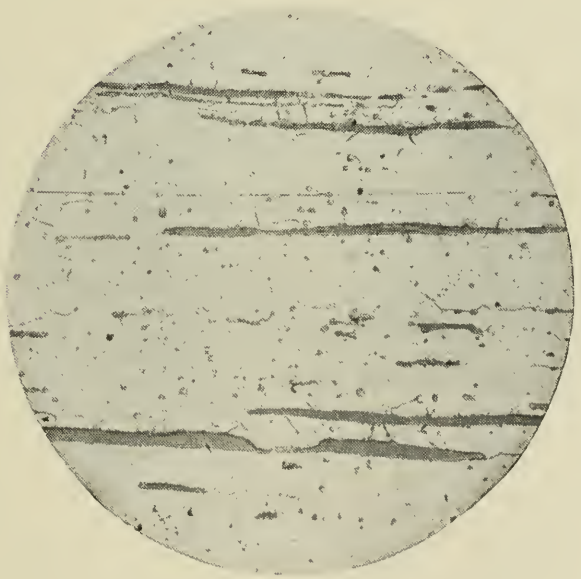

FIG. 167. Wrought iron. (Longitudinal section) (× 100)
Nitol etch. (Photograph by Dr. V. O. Homerberg)

sufficiently high temperature may be maintained to fuse the pig iron. It is constructed entirely of fire brick, incased in a steel shell which is sometimes kept cool by means of circulating water. Silica brick is employed in those parts of the lining which are exposed to the highest temperature. The hearth is basin-shaped and separated from the fire box by a bridge and

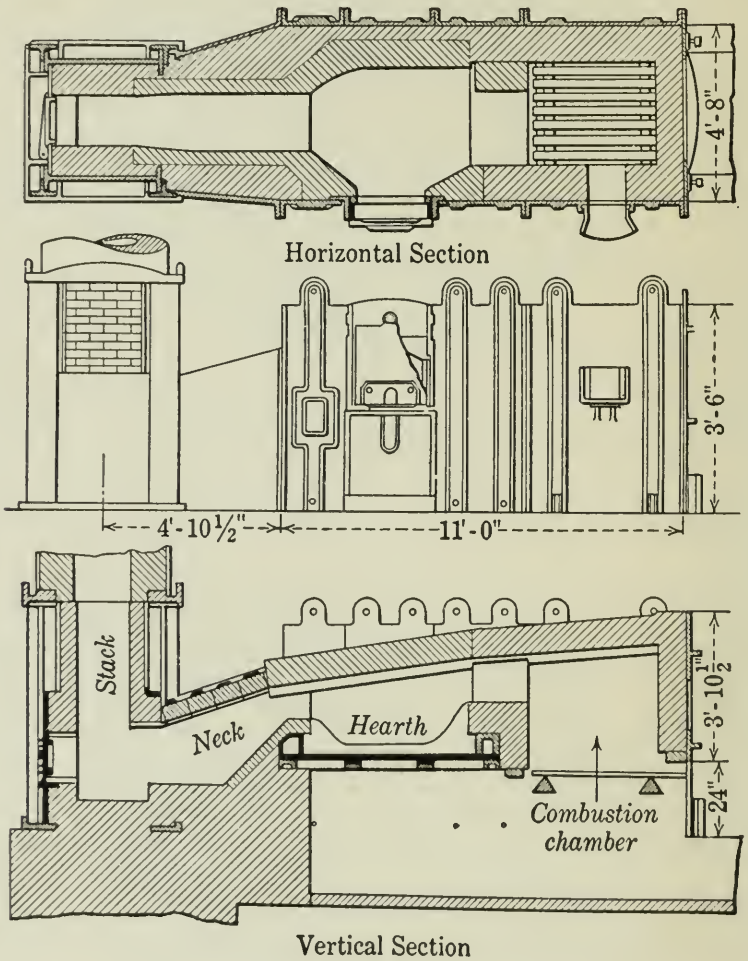

FIG. 168. A puddling furnace

from the neck by a breast wall. Embedded in the hearth are chills (iron castings), through which air or water is circulated in order to prevent excessive corrosion of the hearth. The back wall is solid to the roof; the front wall has an opening about 20 inches square. This opening may be closed by means of a brick-lined sliding door in which is a small hole about 4 inches square, called a rabbling hole. Through this hole the charge may be worked without the necessity of opening the

larger door and chilling the furnace. The hearth is built up by calcining a mixture of roll scale or magnetic oxide of iron and old furnace cinder. By alternate fritting and washing with small charges of iron the hearth is built up into a compact, solid mass. The tools used are paddles, rabbles, and bars of iron.

Operation of Puddling

605. Cycle of operations. The cycle of operations of puddling can be divided into seven distinct periods: charging, melting, clearing, boiling, balling, drawing, and squeezing. The entire cycle will consume from seventy minutes to three hours, depending upon the character of the iron and the skill of the operator.

606. Charging and melting. On the bottom of the furnace, at a high heat from the finishing of the previous charge, is placed 500 pounds of pig iron. The charging door is closed and sealed with some fine coal and the temperature of the furnace is raised by heavy firing. The pigs are turned over with a bar from time to time as they melt. The iron collects on the bottom of the hearth and is covered and protected from excessive oxidation by the slag left from the previous charge. Charging consumes about two minutes; melting, from twenty to twenty-five minutes.

607. Clearing. The operator now stirs the metal at frequent intervals with a rabble. At the end of about ten minutes there will be a distinct change in the appearance of the metal on the hearth. The metal, uncovered by the slag, has a distinct bluish color in marked contrast to the reddish color on first being melted. A fracture test will show a white, or "chill," surface. During this period most of the silicon has been oxidized and unites with the iron oxide of the lining to form a slag. Any adhering dirt is also absorbed by this slag.

608. Boiling. The next step is to raise the temperature and bring on the "boil." While one of the operators works the bath with a rabble the other feeds a little roll scale into the furnace. This lowers the temperature of the furnace, and the charge becomes somewhat pasty. The control of temperature at this point in the process is important, for if a high temperature is maintained throughout the period, the carbon will be eliminated before the phosphorus, and it will be almost impos-

sible to remove the last traces of the latter. The slag is thoroughly stirred into the metal throughout this period, which normally lasts about ten minutes.

The temperature is again raised in order to bring on the boil. It is so termed because of the tiny bubbles of CO which rise to the surface and burn with a characteristic blue flame (puddler's candles). During the first twenty minutes of this period the action is rather vigorous, and since the slag is viscous a great deal of it bubbles out through the puddling hole. As the carbon is removed the melting point of the alloy rises until finally small granules of practically pure iron separate out in the bath.

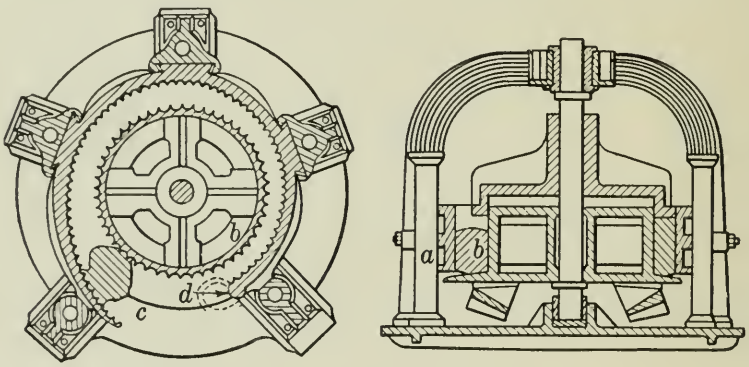

FIG. 169. Rotary squeezer

This can be likened to the crystallizing of salt from an aqueous solution. This separation continues until the whole mass has become stiff and pasty and the bath has "come to nature," as the puddler terms it. The total time of this period is from twenty-five to thirty-five minutes.

609. Balling and squeezing. With a paddle the operator now collects the granules of metal into masses small enough to be easily removed from the furnace. These balls of metal are taken from the furnace with a pair of tongs and carried to the squeezer. Such a piece of apparatus is shown in Fig. 169. It consists of a vertical cogged roll revolving within a stationary cylinder which has a corrugated inner surface. The ball is inserted at one end of the squeezer and comes out at the other. In its passage through the machine the ball is thoroughly worked and kneaded, and most of the slag is ejected. The squeezed ball is then passed on to the rolling mill to be worked down into "muck bar" or other shapes.

Chemistry of the Process

The puddling process is essentially one of oxidation. In order that this may not be too violent, with an excessive loss of iron in the slag, the oxidizing agent employed is mill scale (Fe_3O_4).

610. Silicon. Most of the silicon is eliminated during the melting and clearing stages. The exact mechanism of this change is still a debated question, for it has never been determined whether Fe_3O_4 or FeO supplies the oxygen. According to the latest theories molten iron reduces the Fe_3O_4, thus:

$$Fe + Fe_3O_4 = 4\ FeO,$$

and this FeO oxidizes and slags the Si, thus:

$$Si + 2\ FeO = SiO_2 + 2\ Fe.$$
$$SiO_2 + 2\ FeO = (FeO)_2SiO_2\ (slag).$$

611. Manganese. About one third of the manganese is eliminated during the melting and clearing stages, and the remainder during the boil. The reactions involved are similar to those for silicon, assuming that FeO is supplied in the same manner.

$$Mn + FeO = MnO + Fe.$$
$$2\ MnO + SiO_2 = (MnO)_2 \cdot SiO_2\ (slag).$$

Some of the manganese also goes into the slag as a sulphide when either the sulphur or the manganese in the pig iron is high.

612. Carbon. Very little of the carbon is eliminated during the melting and clearing stages. The reactions involved are

$$FeO + C = Fe + CO.$$
$$FeO + Fe_3C = 4\ Fe + CO.$$
$$Fe_3O_4 + Fe_3C = 3\ FeO + CO + 3\ Fe.$$

All these reactions absorb heat, and therefore none of them take place so long as the temperature of the furnace is kept low.

613. Phosphorus and sulphur. These are the most troublesome elements encountered in the pig iron. About half the phosphorus is eliminated during the melting and clearing stages, the reactions involved being

$$5\ FeO + 2\ Fe_3P = P_2O_5 + 11\ Fe.$$
$$P_2O_5 + 3\ FeO = (FeO)_3 \cdot P_2O_5.$$

The ferrous phosphate is then absorbed by the slag. The remainder of the phosphorus is eliminated in a similar manner during the first part of the boil, when, as has already been explained, the temperature is purposely kept low. Furthermore, unless most of the silicon has been eliminated before the phosphorus, it will reduce phosphorus from the slag.

The operator has very little control over the sulphur. As a matter of fact, unless the manganese is high there may be a slight increase in the percentage of this element, owing to the elimination of the other metalloids. The sulphur content of the pig iron must be kept below 0.03 per cent unless screw stock or some special material is being made.

The chemical history of the puddling process is shown by the following set of chemical analyses:

TABLE LXXIV. REMOVALS IN HAND PUDDLING

SAMPLE	TIME AFTER CHARGING		C	Si	S	P
	Hours	*Minutes*	*Per Cent*	*Per Cent*	*Per Cent*	*Per Cent*
No. 1	0	0	2.275	2.720	0.301	0.645
No. 2	0	40	2.726	0.915	—	—
No. 3	1	0	2.905	0.197	—	—
No. 4	1	5	2.444	0.194	—	—
No. 5	1	20	2.305	0.182	—	—
No. 6	1	35	1.647	0.183	—	—
No. 7	1	40	1.206	0.163	—	—
No. 8	1	45	0.963	0.163	—	—
No. 9	1	50	0.772	0.168	—	—
Puddled bar	—	—	0.296	0.120	0.134	0.139

614. Properties and uses of wrought iron. The tensile strength of wrought iron varies from 46,000 to 50,000 pounds per square inch. Its fibrous structure imparts to it excellent machining qualities, while its superior welding properties, ductility, and resistance to vibration and fatigue render it superior to low-carbon steel. In recent years, however, much of the wrought iron has been replaced by varieties of dead-soft steel. Formerly it was believed that wrought iron resisted corrosion much better than these low-carbon steels, but recent work tends to show that at least a part of this resistance is due to the presence of small amounts of copper and to the purity of the iron. Ingot iron, so called, made in the open-hearth furnace, now appears quite

the equal of wrought iron in this respect. Its chief uses are in bolts, in certain parts of locomotives and machines, and in blacksmithing.

615. Mechanical puddling. Since puddling involves a large amount of hand labor, there have been efforts on the part of all manufacturers to devise some sort of machine to perform this arduous work more cheaply. A discussion of these machines is beyond the scope of this text. They have been none too successful, because of the intricacy of the various motions involved in the operations of charging, stirring, rabbling, balling, etc. Among those that have been tried are circular, flat-bottomed furnaces oscillating about a horizontal axis, oscillating cylindrical furnaces similar to cement kilns, a rectangular furnace that revolves about a horizontal axis, and a cylindrical furnace which both oscillates and revolves about a horizontal axis.

CEMENTATION PROCESS

616. Cement steel. The next logical step in the development of ferrous metallurgy is the manufacture of what is called cement steel. It will be dismissed here with but a brief explanation, for it is now nearly obsolete in this country. Up to the middle of the last century, however, a great deal of the high-grade steel was made by either this or the crucible process.

The raw material is in the form of bars of the best wrought iron, from 6 to 12 feet long and about $2\frac{1}{2} \times \frac{3}{4}$ inches in cross section. Pots are used to protect the bars from the hot gases. The bottoms of these pots are covered with a layer of charcoal about 2 inches deep, upon which bars are laid, flat side down. Alternate layers of bars and charcoal are then charged until the pot is filled. It is then closed and made as nearly air-tight as possible.

The pots are then charged into a furnace and the whole brought gradually to a red heat (from 800° to 1100° C.). This requires about three days, and this heat must be maintained for from seven to twelve days (the time depending upon the size of the bars, the amount of carbon desired in the finished product, and the temperature). When, in the judgment of the operator, this result has been attained, the furnace is allowed to cool and the bars are withdrawn. The surface of the bars is often covered

with small blisters; hence the name *blister steel.* These are formed by the CO resulting from the reaction between the carbon of the charge and the FeO.

Cement steel has one inherent weakness which is not easily overcome. That is the variable carbon content in different parts of the same bar. While the outside of the bar might have a carbon content of 1.1 per cent, and have the requisite hardness, it would be found in working that the pieces as a whole would not have other properties corresponding to 1.1 per cent steel, because the core, or "sap," might be as low as 0.3 per cent C. The penetration of carbon, even at high temperatures, is slow, and within commercial limits of time a piece may never become completely carburized by this method.

THE CRUCIBLE PROCESS

617. General. Since the variable carbon content of cement steel often made it unreliable, the next logical step in the manufacture of steel was to make it perfectly homogeneous by melting, skimming, and casting. In this melting and reworking some of the impurities, as well as the inequalities, are removed so that the crucible process is by no means obsolete. A great deal of our high-grade steel is still made by this process. In England and Germany, where labor is cheaper, the crucible process is still more common.

618. Stock and crucibles. Formerly only cement steel was used for the crucible process, any lack of carbon being made up by suitable additions of this element. Today wrought iron and even scrap steel have entirely superseded this. The use of the latter, however, is to be condemned, for it is much more variable in composition than wrought iron and is likely to contain impurities which cannot be removed by the crucible process. It should be emphasized that the crucible process is essentially one of remelting, not of refining, although a small amount of purification is accomplished. By far the best raw material is high-grade muck bar, which has been sheared into small pieces for careful weighing and charging into the crucibles.

The crucibles themselves are pot-shaped containers with a capacity of from 80 to 125 pounds of metal. In this country they are made of a mixture of graphite and clay; in England,

of fire clay alone. The ordinary proportion in the former case is 60 parts of graphite to 40 parts of a plastic bonding clay. They must be carefully dried and baked in a manner similar to any other refractory. The crucibles vary from 13 to 18 inches in height, from 8 to 13 inches at the larger diameter, with a wall thickness of $1\frac{1}{2}$ inches at the bottom and $\frac{3}{4}$ inch at the top. They will last from ten to twenty heats under ordinary conditions.

619. The melting furnace. A typical American crucible furnace is shown in Fig. 170. It is gas-fired and of the regenerative type, since a very high temperature must be maintained over considerable periods. Each of the melting holes is about 3 feet deep and large enough to hold from four to six crucibles comfortably. The bottom of the melting hole is protected with a layer of finely divided coke from 6 to 8 inches deep. The mouth of the melting hole is kept covered with a heavy fire-brick-lined cover during the entire melting operation. The workmen stand on the floor above the regenerative chambers. When producer gas is used, about one ton of coal is required for each ton of refined steel turned out.

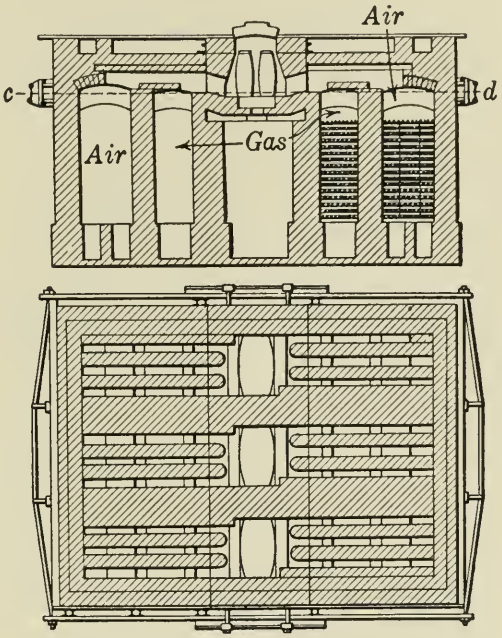

FIG. 170. A crucible furnace

OPERATION

620. Cycle of operations. The raw material, sheared muck bar, scrap tool steel, or low-carbon scrap, as the case may be, is carefully weighed out, together with the necessary recarburizer or iron alloy to make the desired grade of steel. This material is charged into the crucible with the wrought iron or scrap on the bottom to prevent segregation of some of the heavier alloying agents. The crucibles are covered and lowered into the melting hole. At the end of from two and a half to four hours,

depending upon the heating conditions and the carbon content of the charge, melting will be completed. During this time the pot is inspected at frequent intervals, for it is necessary that the metal be as free as possible from all solid and gaseous inclusions. Such purified steel is termed dead, and the period of from thirty to forty minutes during which it is being purified is called the killing period. The gases gradually escape, while the solid inclusions in the form of slag can be removed by swabbing the surface of the melt with a ball of cold slag on the end of an iron bar.

The pot is then removed from the furnace, and the contents are poured into a cast-iron mold. Sometimes a little stick aluminum is added to effect more nearly complete deoxidation. Usually the above mold is 3 or 4 inches in cross section and long enough to hold a single potful, but sometimes several pots may be poured into a steel ladle and the bar teemed from the bottom of the ladle. The bars are then stripped, inspected, and made ready for market.

Chemistry of the Crucible Process

621. Chemistry. The chemistry of this process is very simple. A reducing atmosphere is maintained in the furnace, so that, after melting, all the oxide of iron is in the ferrous condition. This oxide reacts with the silica of the crucible to form a slag which covers and protects the steel. Any gaseous inclusions rise to the surface and escape. The carbon added to the charge reduces any other oxides, and these metals join the steel. The excess carbon (calculated) is dissolved in the metal to give a steel of the desired composition. All segregations disappear, and at the end of the killing period we have a limpid bath of steel, free from all inclusions.

THE ACID BESSEMER PROCESS

622. General. The fact that cement steel was not homogeneous, and that both cement and crucible steel were expensive, owing to the large amounts of hand labor employed and the low tonnages handled, soon led the metallurgists to seek a cheaper and quicker way of making steel. It may be said that the present industrial development of the world did not start

until 1856, when Sir Henry Bessemer discovered the process which bears his name. Although not the best by any means, it is the simplest process yet devised for making steel.

Briefly, it consists of blowing air, under pressure, through a molten mass of pig iron contained in a vessel called a converter, similar in principle to the converter already described in connection with the metallurgy of copper. The air in its passage through the molten mass oxidizes the silicon, manganese, and carbon of the steel. The carbon escapes as a gas (CO), and the silicon and manganese are oxidized to their respective oxides and unite with the refractory lining of the vessel to form a slag which floats on top of the metal. At the end of the blowing period, which normally lasts about fifteen minutes, the slag is skimmed off, the converter is emptied into a ladle and made ready for another charge. Thus is accomplished in these few minutes what would take hours or even days to accomplish in either the crucible or the cementation process.

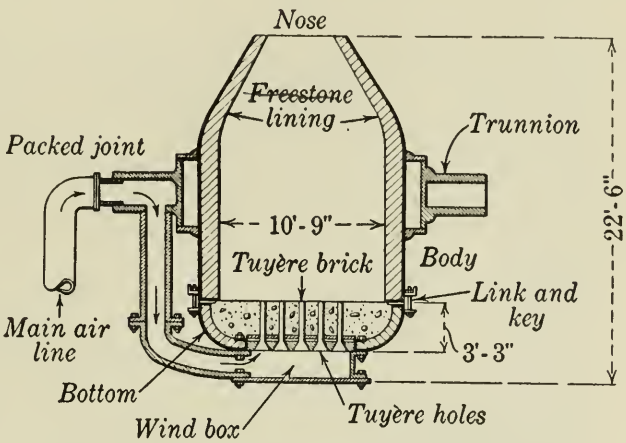

FIG. 171. An acid Bessemer converter

623. The converter. A large steel converter is shown in Fig. 171. It consists of three parts, — nose, body, and bottom. They are all made of heavy steel plates, and the three are joined together by means of bolts and keys so that the individual parts may be easily and quickly removed for repairs. The whole is held in position and may be rotated about heavy trunnions, which in turn are supported on columns. Both the trunnions are hollow, one being connected, by means of a packed joint, with the main air line. By this means the air can be supplied to the converter while it is being tilted to any position. The pressure of air employed is only that sufficient to overcome the head of molten metal in the converter, ordinarily from 10 to 20 pounds per square inch. A valve is also provided for introducing steam as the condition of the charge warrants.

To the other trunnion is fastened a pinion which engages a toothed rack, in turn operated by a hydraulic cylinder. By this means the converter may be turned to or held in any position. If the air is admitted through the bottom, it is termed a bottom-blown converter; if through the side, a side-blown converter. It may be termed concentric or eccentric, depending upon whether the mouth is in a plane parallel to the bottom.

The converter body is lined (in the acid process) with any high-grade siliceous refractory. Usually a variety of siliceous

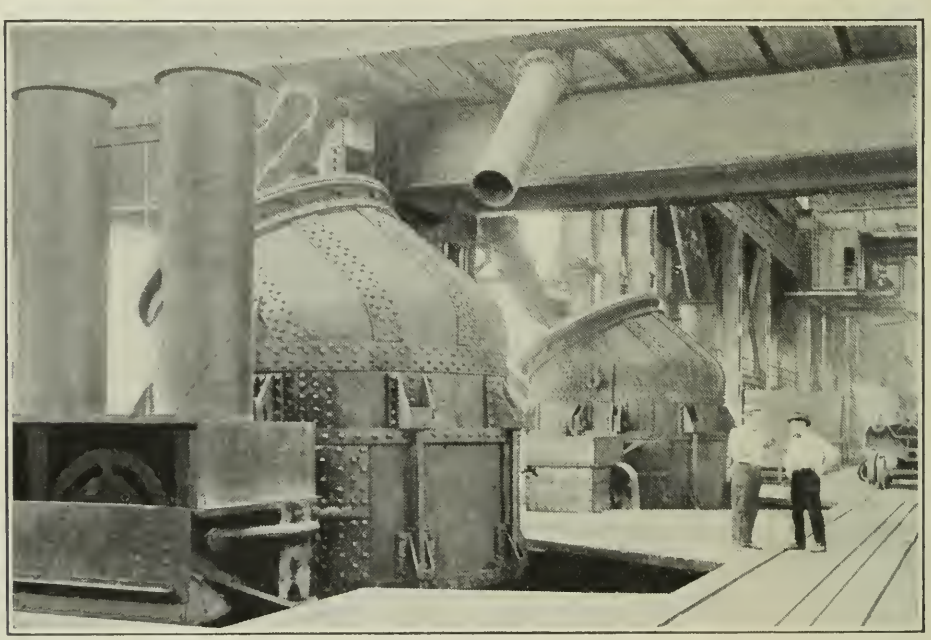

FIG. 172. Bessemer converters

sandstone called freestone is used. The lining is built of blocks of this material and cemented in place with fire-clay cement. The thickness will vary from 10 to 16 inches, being thinnest in the nose and thickest in the body, where it is subjected to the greatest wear. When the lining is complete, it is plastered with ball clay and thoroughly dried. Its life will vary from six weeks to five months.

The converter bottom is lined separately from the body. The wind box is made up of heavy steel plate with a flat circular casting closing the top. This casting has about twenty holes for the tuyères. Special tuyère bricks (each 30 inches long and 7 inches in diameter, with twelve half-inch holes parallel to the longer

axis) are placed over the tuyère holes, and the space between is filled in with large bricks. A mixture of ganister and fire clay cements the whole together when it has been dried and baked. Each converter has several of these bottoms ready, for their life is seldom more than twenty heats and it is necessary to change these bottoms in as short a time as possible so as not to interfere with the operation of the plant as a whole. The bottom can be changed by running under the converter a specially built car carrying a powerful hydraulic jack. This jack relieves the pressure on the bottom so that the supporting keys may be knocked out and the bottom lowered and taken away for repairs. When a new bottom or lining is put in place, it is necessary to bring the converter to heat with gas or oil fires.

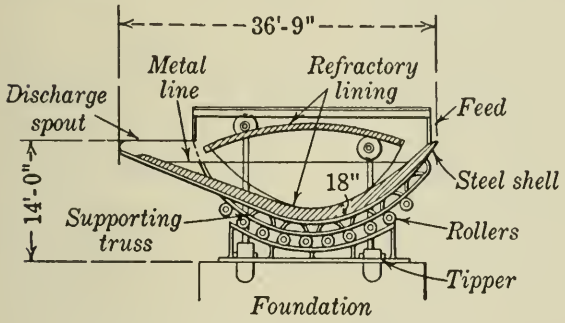

FIG. 173. A mixer

624. The mixer. This is an important part of either a Bessemer or an open-hearth plant; so it may well be described now. A large mixer is shown in Fig. 173. It consists of a large cylindrical vessel, lined with high-grade refractory, and mounted on rollers so that it may be completely emptied if desired. At one side of the mixer is an opening for charging the hot metal, and at the diagonally opposite end another opening from which this metal may be drawn as required by the plant. The capacity of such mixers ranges from 200 to 1500 tons. While they are capable of keeping the metal molten for long periods of time without the application of outside heat, it is customary to heat the contents by introducing an oil-burner into the discharge opening. The mixer has several very important advantages:

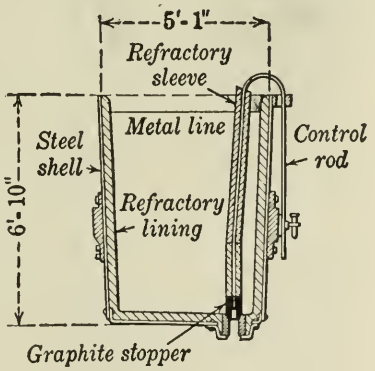

FIG. 174. Ladle and stopper

1. It renders the Bessemer or open-hearth plant independent of irregularities and accidents to the blast furnace by serving as a reservoir for the molten metal.

2. It renders the chemical composition of the iron more nearly uniform, the slight variation of a single tap being absorbed by the larger mass in the mixer.

3. Some desulphurization takes place in the mixer.

4. It conserves the heat of the molten iron.

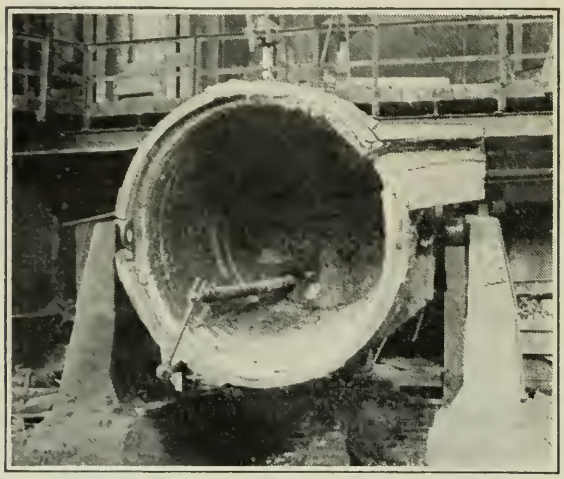

FIG. 175. Ladle and stopper

625. An ingot-casting equipment. A teeming ladle for the casting of ingots is shown in Fig. 174. It is a large, cup-shaped container, lined with about $2\frac{1}{2}$ inches of refractory brick and fitted with a teeming hole in the bottom. This hole can be closed by means of a graphite stopper head, and the flow of metal thus controlled.

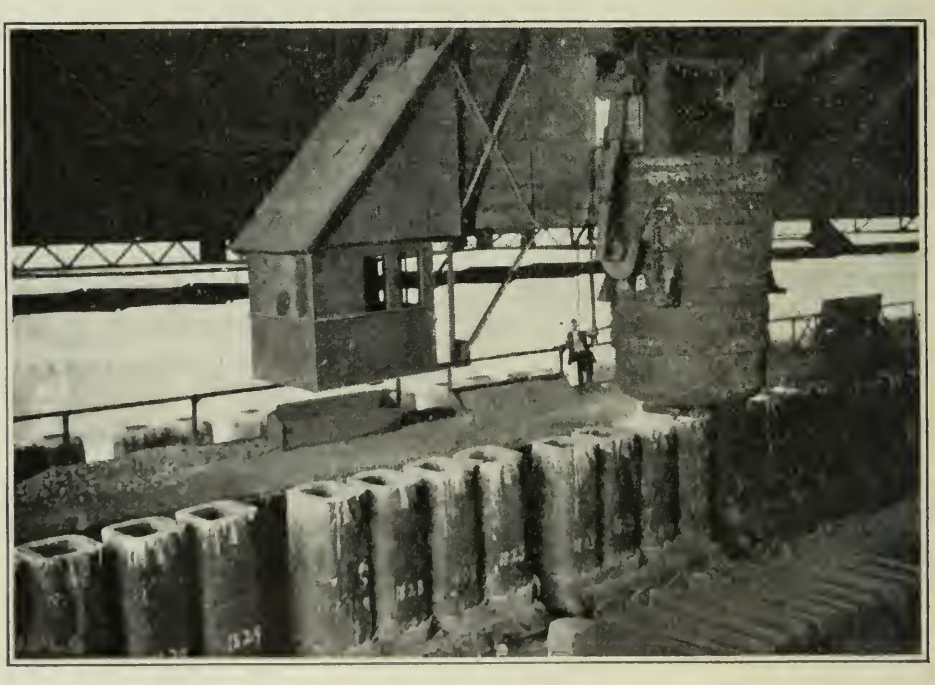

FIG. 176. Teeming ingots

By this means the slag, which floats on top of the metal, is kept out of the ingots. These ladles will hold from 5 to 25 tons, depending upon the size of the converter to be served.

The ingot molds are of cast iron, about 6 feet high and 24 inches square. They are open at both ends and are supported (for casting) on heavy cast-iron plates called stools. Two of the ingots are thus mounted on each car or buggy. The ingots are rounded at the corners and have a slight taper in the direction of the longer axis in order to facilitate stripping. The inside of the mold must be kept smooth and clean if it is to yield perfect ingots. The inside of the mold is often given a coat of whitewash between casts. Its life is ordinarily about seventy casts. A stripper is shown in operation in Fig. 177. Sometimes the molds can be easily pulled off the ingots. More frequently, however, scabs and imperfections cause them to stick. With this machine the ingot can be held in position on the stool by means of the central ram, or plunger, while the ingot mold is pulled away from it by means of the outside jaws.

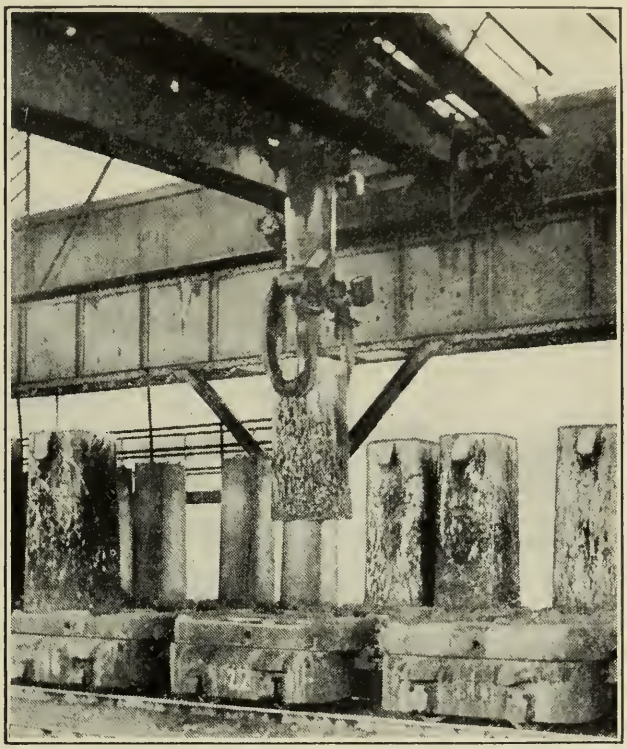

FIG. 177. A stripper

OPERATION OF THE BESSEMER PROCESS

626. Cycle of operations. For the purpose of this discussion the process will be divided into four periods: charging, blowing, recarburizing, and teeming.

627. Charging. The desired weight of pig iron, let us say 15 tons, is ordered from the mixer. The converter is meanwhile racked down into a nearly horizontal position so that the tuyères will be clear of the metal. The iron is poured into the

converter from a ladle. If it is too hot, a small amount of cold scrap may be added. It is very important that the blower know the approximate composition of the metal, in order to conduct the blow intelligently. The temperature of the bath is entirely dependent upon the initial temperature and the amounts of Si, C, or Mn in the steel. The advantage of the mixer is at once apparent. The blower knows that his next order of metal, irrespective of what the blast furnace has produced meanwhile, will not differ markedly from the last, and he can be guided by the behavior of that in the converter.

628. Blowing. As soon as the molten metal and scrap have been added, the blast is turned on and the converter is racked into the upright position. The blast pressure is adjusted; for if it is too low iron will find its way into the tuyères, and if it is too high there will be an excessive loss of metal thrown out of the converter. By the appearance of the flame, as viewed through colored glasses, the blower can judge the condition of the metal in the converter. For the first five or six minutes dense brown fumes, followed by a dull-red, short, pointed flame, issue from the converter. During the next eight minutes this flame lengthens steadily up to about 30 feet, and a dull roaring sound comes from the converter. With the elimination of the carbon the flame begins to drop, or die, becomes less luminous, and, through the colored glasses, is streaked with purple. The charge is usually "turned down," or emptied, at this point, which corresponds to from 0.03 to 0.10 per cent C; but it may be blown dead, in which case the flame will disappear entirely. Slag is skimmed off the converter, — once if the metal is low in impurities, more often if it is high in impurities.

The blowing of a converter is an exceedingly delicate operation, considering the scale on which it is carried out. If it is not blown to the proper point, recarburizing yields a steel which does not conform to the specifications from the rolling mill; if it is blown too far, there is, in addition to the danger of freezing the converter, that of introducing an excessive amount of FeO into the metal. To raise the temperature of the bath the following methods are available:

1. The addition of ferrosilicon, the oxidation of the silicon furnishing the heat.

2. Tipping the converter so as to expose a few tuyères. Heat in this way is furnished by the CO gas from the bath burning just above it.

3. Adding high-silicon pig iron from another mixer.

High temperatures, which are far more common, can be corrected by one of the following methods:

1. The addition of cold steel scrap.

2. Tilting the converter, shutting off the blast and allowing the contents to cool.

3. The injection of steam.

629. Recarburizing. This is a very important step, for on it depends the success of the steel-making operation. It has the double function of putting certain elements into the bath and taking certain others out. This second function is of peculiar importance, for it will be recalled that it was not until methods were devised for removing the oxygen from Bessemer steel that such material came into general use. The dropping of the flame indicates that all the silicon and all except small amounts of manganese and carbon have been eliminated. At this point the proper amount of molten recarburizer is added, either to the converter just before pouring or to the ladle just after. The character of the recarburizer will depend entirely upon the kind of steel being treated. The recarburizers in common use are given in the following table:

TABLE LXXV. DEOXIDIZERS AND RECARBURIZERS (IN PER CENTS)

	Fe	C	Mn	S	P	Si	Ash
Ferromanganese	11.95	6.50	80.40	Trace	0.160	1.00	—
Spiegel	73.20	5.00	20.40	Trace	0.100	1.10	—
Ferrosilicon	86.70	2.00	0.50	0.05	0.080	10.60	—
Pig iron	93.05	4.50	0.67	0.047	0.088	1.67	—
Anthracite	—	85.50	—	—	—	—	4.50

The amount added must be carefully calculated, with due allowance for loss in the converter or the ladle. The converter is then inverted in order to throw out the last of the slag and make it ready for the next heat.

630. Teeming. The ladle, full of steel from the converter, is now ready to be cast into ingots. It is covered with a thick layer of congealed slag. The ladle is transferred, on a small flat car,

to the teeming train and lifted by a heavy crane to the teeming table. A number of ingot molds are ready on the track. By means of an automatic device each mold can be moved from under the ladle as it is filled and another put in its place. At some plants the ladle is moved by the crane, and the ingot molds are stationary. Into each ingot is thrown about four ounces of stick aluminum to deoxidize the steel. In the case of "wild" (gassy) steel it may be necessary to use more than this amount. The flow of metal can be controlled at will by raising or lowering the stopper in the ladle. The last of the metal, together with its covering of slag, is rejected. When the ingots have cooled sufficiently, they are taken to the stripper, the molds are removed, and the ingots are sent on to the soaking pits, where they are reheated for rolling.

Chemistry of the Acid Bessemer Process

631. Chemistry. The reactions involved in the acid Bessemer process are simple and easily understood. The metal in the converter may be considered as a solution, in iron, of Si, Mn, C, P, and S, with iron, of course, greatly in preponderance. When the blast of air enters this mass, the iron is oxidized, thus:

$$2\,Fe + O_2 = 2\,FeO + 131{,}400 \text{ calories.}$$

The FeO, as well as the air, then serves as a vehicle to carry the oxygen to the other impurities. Silicon and manganese are next oxidized, thus,

$$2\,FeO + Si = SiO_2 + 2\,Fe + 64{,}600 \text{ calories,}$$
$$FeO + Mn = MnO + Fe + 25{,}200 \text{ calories,}$$

and the oxides formed react with the silica of the lining to form a slag, thus:

$$FeO + SiO_2 = FeO \cdot SiO_2 + 9300 \text{ calories,}$$
$$MnO + SiO_2 = MnO \cdot SiO_2 + 5400 \text{ calories.}$$

A little carbon may be eliminated along with the silicon, thus,

$$2\,C + O_2 = 2\,CO + 58{,}320 \text{ calories,}$$
$$FeO + CO = Fe + CO_2 + 2340 \text{ calories,}$$

but most of the carbon is eliminated later.

As soon as most of the manganese and silicon have been oxidized, the following reactions start:

$$FeO + C = Fe + CO - 36{,}540 \text{ calories.}$$
$$FeO + Fe_3C = 4\,Fe + CO - 45{,}000 \text{ calories.}$$

This is due to the rise in temperature of the converter through the oxidation of the manganese and silicon and the formation of the slag.

The phosphorus and sulphur, under normal blowing conditions, are not affected at all. Actually there is often a slight increase in these constituents, owing to the removal of the other impurities.

Recarburizing is accomplished by the simple dissolving of the carbon by the steel. An excess must be added, for some is burned in the air and some oxidized by the FeO, thus:

$$FeO + C = Fe + CO.$$

Deoxidation is accomplished largely by the manganese and silicon, thus:

$$FeO + Mn = MnO + Fe.$$
$$2\,FeO + Si = 2\,Fe + SiO_2.$$
$$SiO_2 + FeO = FeO \cdot SiO_2.$$

The oxides thus formed are dissolved in the slag.

THE BASIC BESSEMER PROCESS

632. The converter. Mechanically the vessel in which the basic process is carried out is much the same as the one used in the acid process. The lining, however, instead of being of siliceous material, is made up of calcined dolomite held together with about 10 per cent of tar and firmly rammed into place. It is not desired that it react with the constituents of the bath; so lime is added to the bath before the beginning of the blow. This will react with the SiO_2 to form a basic slag and thus protect the lining.

633. Chemistry of the basic process. The elements are removed in much the same order and manner as in the acid process, but there is a slight difference in the rate. Because of the fact that the operation is carried out with a basic slag, the silicon is removed more rapidly and the manganese less

rapidly than in the acid process. The carbon is removed after the silicon, while the phosphorus is not affected to any great extent until after most of the carbon has been removed. The reactions involved are much the same as in the acid process.

There is one great difference between the two processes, however, — in the afterblow. This is the period during which the phosphorus is most rapidly eliminated. It can best be shown by a graph, as in Fig. 178. Following the course of the phosphorus in this graph we see that the percentage is little affected until the ninth minute (after the removal of most of the carbon), when it drops off rapidly and is practically eliminated in three more minutes of blowing. It goes into the slag as $(CaO)_4P_2O_5$. The basic slag used favors the absorption of sulphur; so a small but variable amount of this goes into the slag as CaS.

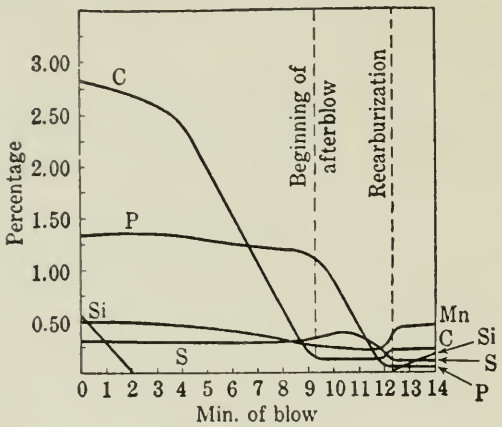

FIG. 178. The basic Bessemer process

The slag from this process contains a large percentage of phosphorus; so the metal must not be carburized in the converter. If this were done, the phosphorus would be reduced by the recarburizer, thus,

$$(CaO)_4 \cdot P_2O_5 + 4\ SiO_2 = 4\ CaO \cdot SiO_2 + P_2O_5,$$
$$2\ P_2O_5 + 5\ Si = 5\ SiO_2 + 4\ P,$$

and thrown back into the metal. Ordinarily most of the slag is poured off and the rest of the slag held back while the recarburizing metal is being poured into the converter. With such a thin covering of slag the rephosphorization may be small.

634. Advantages and disadvantages of the basic process. This process finds its chief use in districts producing pig iron that is very high in phosphorus. In order that the process may be conducted with safety there must be at least 1.75 per cent of phosphorus in the pig iron; and since we produce small tonnages of such iron, the process is of little importance in this country. It is safe to say, however, that large amounts of this

element can be eliminated more cheaply in the basic converter than in the basic open-hearth process. On the whole, operating costs are high, for the following reasons:

1. The blows are about 30 per cent longer than in the acid process.
2. There is more slag to be handled.
3. The basic lining is much more costly.
4. Fluxes must be added to form the slag.

INGOT-MAKING

635. General. Perhaps the most important step in the manufacture of steel is the teeming of the ingot. The reduction of the iron in the blast furnace and its purification in the Bessemer converter or open-hearth furnace may be carried out with great care, and yet the steel be ruined in the few minutes of teeming. Such improperly teemed steel can be recovered only by sending it back for further purification; no amount of rolling, working, or heat treatment will ever remedy the defects. If not entirely ruined it may be necessary to discard as much as 25 per cent of the ingot as scrap in order to yield a clear, homogeneous piece for rolling or shaping. The finishing of the ingot takes about thirty minutes, — less than 5 per cent of the total purification period. The actual solidification (a most important step) requires relatively inexpensive equipment, such as teeming ladles, molds, stools, etc. Yet until a few years ago most of our unsound steel could be traced to this short, inexpensive step. It is not logical to spend hours of time and use equipment costing hundreds of thousands of dollars to purify steel and then spoil it in a few minutes for lack of proper methods involving the investment of a relatively insignificant sum. A great deal of research has been conducted along the lines of teeming and ingot solidification, but general ingot-making practice is still far from satisfactory; witness the fact that in the manufacture of tin plate, because of imperfections in the steel, 10 per cent of "wasters" is considered good practice, and as much as 25 per cent is sometimes encountered. The chief defects in steel, owing to the casting of the ingot alone, are as follows: (1) pipes; (2) blowholes; (3) segregation; (4) ingotism; (5) checks and scabs; (6) nonmetallic inclusions; (7) butt cracks.

636. Size of ingots. The size of the ingot will depend upon the use to which it is to be put, although it is obvious that it will cost less to teem a 100-ton open-hearth heat into 4-ton ingots than into 2-ton ingots. Ingots range in size from $9 \times 9 \times 48$ inches up to $2 \times 2 \times 8$ feet, and in weight from 1000 pounds up to 10,000 pounds or more. Ordinarily ingots are square or rectangular in cross section, with rounded corners. The larger ingots may be round with a corrugated or fluted surface. There is a small taper on the ingot to facilitate stripping. An ingot described as 18×21 inches has these dimensions at the butt end. The ingot molds are open at both ends; the lower end, when in use, is closed by the stool upon which it is mounted.

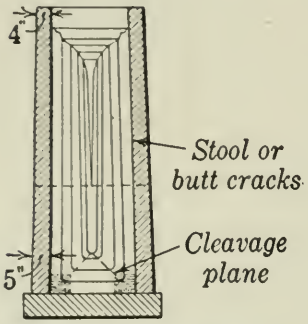

FIG. 179. A standard mold

Big end down without top

FIG. 180. A standard rail ingot

Big end down

637. Pipes in a standard mold. As soon as the molten metal is poured into the mold, the metal next to the mold and that next to the stool is chilled by contact with the cold surfaces and starts to solidify as a skin. Freezing of the molten metal then progresses as indicated by the contour lines of Fig. 179. Since there is a certain volumetric shrinkage in any steel as it passes from the molten to the solid state, the molten top of the ingot will drop in following this shrinkage and finally form a shrinkage cavity, or "pipe," as shown. Fig. 180, a split ingot poured in a standard mold, shows the extent of this piping. Fully 50 per cent of this ingot must be cropped off and returned to the process as scrap if a homogeneous piece for rolling is desired. This is an extreme case; ordinarily the waste is much less than

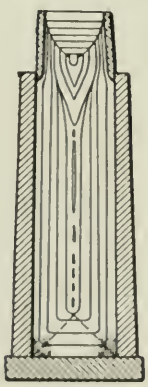

FIG. 181. A standard mold

Big end down with hot top

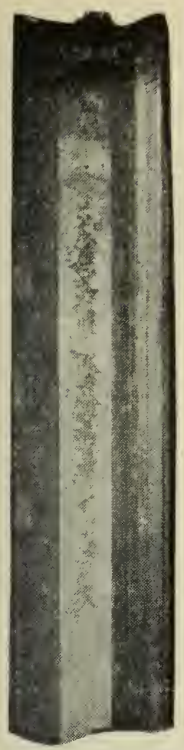

FIG. 182. A standard ingot

Big end down with hot top

this, but seldom less than 10 per cent. Subsequent rolling or working will not close up these cavities, for the rolling temperature is always well below that of welding, and in addition the surfaces of these cavities are covered with an oxide of iron. In order to keep the top of the mold hot and thus furnish a supply of molten metal to the congealing bottom part, some operators have tried the hot-top mold. By means of a special refractory top the heat is conserved, and cooling then progresses as shown in Fig. 181. This cuts down considerably the large pipe, as shown in the split section in Fig. 182, but it is apt to cause the formation of secondary pipes.

638. Pipes in big-end-up ingots. The Gathmann mold, the invention of Emil Gathmann, is an attempt to cut down piping by casting the ingot in the reverse position, — the big end of the ingot at the top. By varying the thickness of the walls and using a refractory top, differential cooling causes the top to remain liquid until the bottom has entirely solidified. At the bottom, or lower portion, the chill ratio is approximately 3 to 1; at the upper end it is about $1\frac{1}{2}$ to 1. Freezing in this type of ingot will progress as indicated by the contour lines of Fig. 184. The top is kept molten by the refractory sink head and acts as a reservoir to feed metal to the lower part of the solidifying ingot. The pipe is thus confined to the relatively small top, which can be cropped off and discarded. Fig. 183, a real photograph of a split ingot cast in a Gathmann mold, bears out this theory.

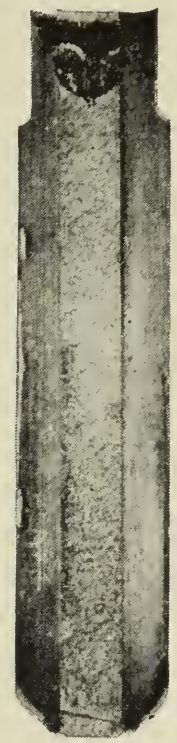

FIG. 183. A Gathmann 20-inch ingot

Note solid fracture below sink head

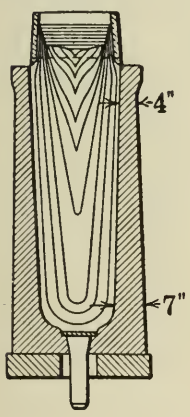

FIG. 184. A Gathmann mold

With hot top

639. Blowholes. Molten steel is a solution, and as such it is capable of dissolving, besides solid elements such as carbon, nickel, and manganese, large volumes of gases such as nitrogen, hydrogen, and carbon monoxide. Following the laws of solutions, as the ingot cools in the mold these gases are thrown out of solution. The ingot at this stage is a viscous mass, so that a large part of the gas is unable to escape but is held in the ingot as bubbles or after solidification as blowholes, or cavities. These may vary in size from microscopic pores up to cavities $\frac{1}{2}$ inch or more in diameter. Whatever the size, they constitute a weakness in the steel, for the walls are usually oxidized and will not weld together in subsequent mechanical treatment. It is common practice to use "open," or "effervescing," steel for certain purposes. This is steel in which the purifying reactions have not been carried to completion in the furnace, and the gases as they come out of solution tend to equalize the natural contraction of the cooling mass and thus cut down the size of the pipe. This remedy is just about as bad as the disease which it is intended to cure. The only way to eliminate blowholes is to see that the steel before it is teemed is completely deoxidized and degasified.

640. Segregation. Since steel is an igneous solution of various compounds, elements, and gases in liquid iron, it should obey the laws of solution. Within certain limits it does do this. These compounds or elements have different freezing points; some of them freeze at a lower temperature than iron. They tend to form eutectics and to concentrate these impurities in the remaining liquid. This concentration of certain impurities in the solid ingot is called segregation. The last bit of liquid steel to solidify (of lowest melting point) will contain more of these impurities, and this separation will take place along the center line of the ingot (often referred to as the "line of segregation"), and is at a maximum at the bottom of the pipe. Rapid cooling, in preventing movement within the cooling ingot, tends to cut down this segregation. The tabulation on the following page, which gives (in per cents) analyses of samples from various parts of the interior of an ingot, shows this segregation. Unless the pipe is cut off and discarded, there will be similar variations in the composition of the finished product.

	C	Mn	P	S
	Per Cent	*Per Cent*	*Per Cent*	*Per Cent*
Ladle analysis	0.51	0.50	0.022	0.031
Sample cut 1 inch from surface at middle of ingot	0.52	0.48	0.026	0.034
Sample cut at center of ingot	0.50	0.48	0.029	0.038
Sample cut on center line of ingot 4 inches from bottom of pipe	0.78	0.52	0.092	0.136
Sample cut on center line of ingot 2 inches from bottom of pipe	0.84	0.52	0.108	0.178

641. Ingotism. Ingotism, or coarse crystallization, is another serious defect in ingots. It is common knowledge that slow cooling of aqueous solutions tends to promote the formation of very large crystals. The same is true of igneous solutions, and these large crystals, once formed, with relatively long cleavage planes, make the metal weak. Such metal is very likely to tear in rolling. Quick cooling tends to prevent ingotism.

642. Checks and scabs. These are really minor defects, for by careful work they may to a large extent be avoided. If the surface of the mold is rough, transverse cracks, or checks, are developed in the natural cooling of the ingot. The metal catches in these rough spots, and the tremendous strain set up in cooling is sufficient to disrupt the metal. The surfaces of these cracks become oxidized, forming seams in the finished product. Improper pouring, the metal being splashed against the cold sides of the mold, often causes scabs.

643. Nonmetallic inclusions. Slag inclusions may be due to an improperly finished heat or to slag caught in the steel during teeming and stirred into the mass. The steel, being close to its freezing point, is viscous, and in the short time elapsing between pouring and actual solidification the slag particles cannot rise through the viscous mass. Particles of dirt from the ladles or old molds may be entrained in the same manner.

644. Butt cracks. The standard ingot, in solidifying, owing to progressive growth from perpendicular surfaces, tends to form cleavage planes, as indicated in Fig. 179. Another defect is butt cracks, caused by the steel catching or binding to the mold bottom. At least this appears to be the cause, for they can be eliminated by rounding the bottom of the ingot mold.

645. The Gathmann mold. The Gathmann mold in common use today takes the form illustrated in Fig. 185. The bottom,

besides having a two-plug closure, has a tapered contour to prevent the formation of butt cracks. The upper, or refractory, plug in the bottom is intended to receive the impact of the molten metal as it issues from the teeming ladle and thus to prevent cutting or scarring of the walls of the mold bottom. This plug is seated in a recess so as to prevent lateral movement. The bottom, or metallic, plug is used as an ingot lifter or stripper in case the ingot sticks to the mold. Any refractory material can be used for the hot-top, or sink-head, casing. Carbonaceous material such as graphite, although it might have a long life, would give up carbon to the metal. The one in most common use is the Chapin, composed of waste blast-furnace slag with a suitable binder in order that it may be molded and baked in the proper shape. In stripping, the hot top is removed and a crane pulls the ingot (when completely solid) out of the mold by means of the protruding upper end, or the mold may be upset and the ingot dumped out.

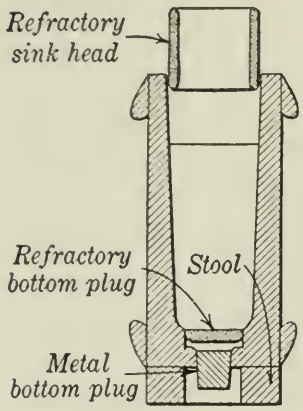

FIG. 185. A Gathmann mold

THE BASIC OPEN-HEARTH PROCESS

646. General. The Bessemer process, although it is quick and cheap, is unsatisfactory for a number of reasons. The steel is likely to contain a good deal of dissolved gas or FeO, and hence be unreliable or weak. The operator has but little control over the metal once it is in the converter, and a very short time in which to make any adjustments. The process does not remove phosphorus or sulphur, and hence is unsuited to iron containing large amounts of these elements. Such objections led metallurgists to seek other means of purifying pig iron. The present open-hearth process was invented by Henry Siemens in 1858. Briefly, the furnace consists of a basin-shaped, rectangular hearth in which the pig iron is melted. At either end of the furnace are regenerative chambers for preheating the gas and air, since a very high temperature is necessary to keep the metal and slag liquid. It would be difficult, if not

impossible, to obtain such a degree of heat with a simple coal-fired furnace. The gas and air currents are reversed every twenty minutes. Reagents in the shape of flux and iron ore are added through doors in the side of the furnace.

The Basic Open-Hearth Furnace

647. Importance. Since this process is fast becoming our most important steel-making process, the furnace used warrants a rather detailed description. Table LXXVI shows the rapid strides made by this process in the last few years, the reasons for which will be apparent later.

Table LXXVI. Production of Steel Ingots and Castings (in Tons of 2240 Pounds)*

Year	Acid Bessemer	Acid Open-Hearth	Crucible and Electric	Basic Open-Hearth	Total
1910 . .	9,412,772	1,212,180	174,444	15,292,329	26,091,725
1915 . .	8,287,213	1,370,377	184,721	22,308,725	32,151,036
1920 . .	8,883,087	1,296,172	577,952	31,375,723	42,132,934
1921 . .	4,015,938	507,238	178,057	15,042,564	19,743,797
1922 . .	5,919,298	921,812	374,645	28,387,171	35,602,926
1923 . .	8,484,088	1,234,636	559,951	34,665,021	44,943,696
1924 . .	5,899,590	857,827	454,999	30,719,523	37,931,939
1925 . .	6,723,962	947,146	635,074	37,087,342	45,393,524
1926 . .	6,948,449	1,024,783	667,216	39,653,315	48,293,763
1927 . .	6,191,727	924,067	675,123	37,144,268	44,935,185

648. The open-hearth furnace. A modern open-hearth furnace is shown in Fig. 186. It consists of a rectangular hearth about 15 feet wide and 40 feet long inside. It is deep enough to accommodate a bath of metal and slag from 20 to 24 inches deep and is rated at a capacity of 100 tons per heat. It is made up by laying about 24 inches of fire brick on a heavy concrete foundation. The fire brick is heavily reënforced with steel I beams, for the stresses involved, when the hearth is full of metal, are considerable. On top of the fire brick is laid about 9 inches of magnesite brick. When the rest of the furnace is erected and ready, a 10-inch bottom of grain magnesite and basic slag is sintered into place, about $\frac{1}{4}$ inch at a time. In this way an extremely strong bottom is built up to resist the pres-

* Mineral Industry.

sure of the metal. Since the life of a furnace is determined partly by the life of the bottom, the construction of this warrants great care. The back wall of the hearth is provided at its upper edge with a slag hole for removing the bulk of the

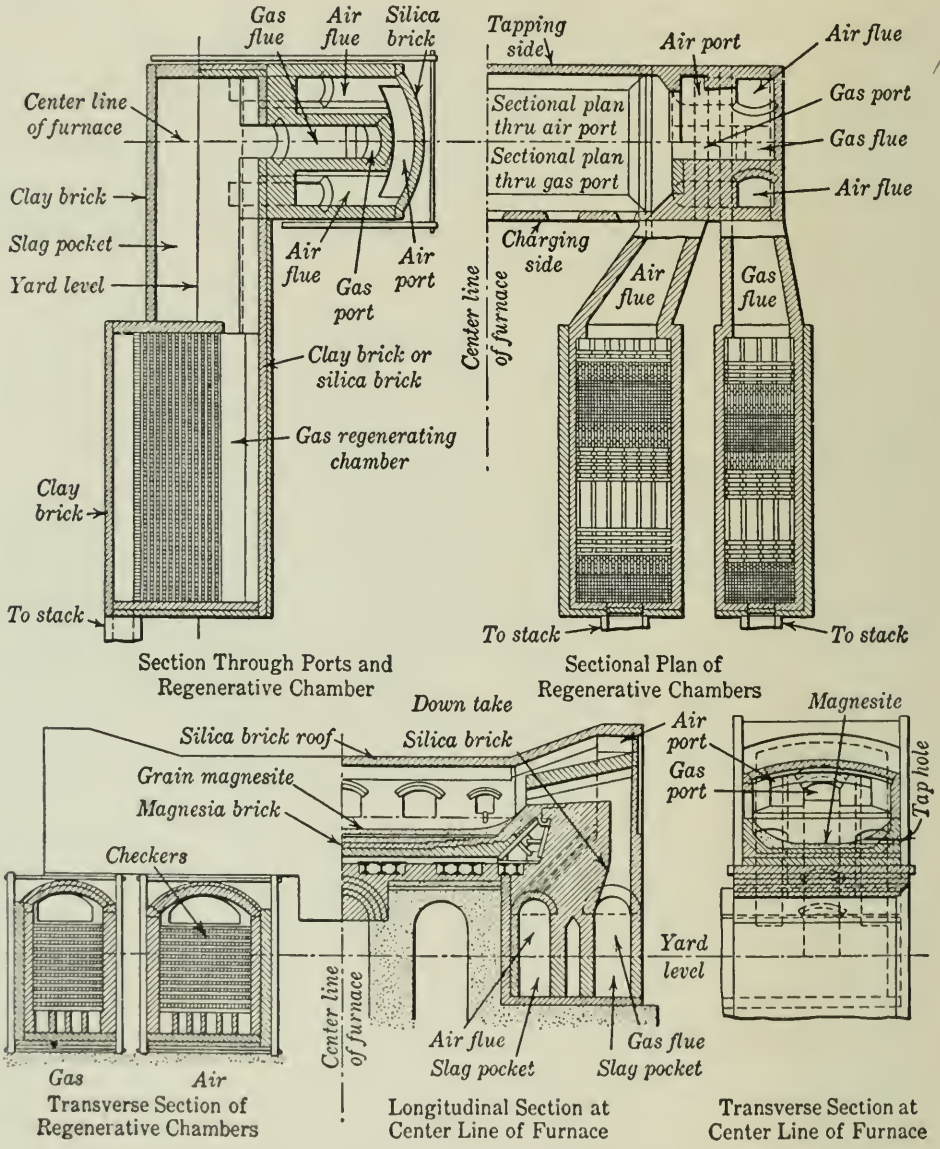

FIG. 186. Open-hearth furnace

slag. A tapping hole for the metal, about 8 inches in diameter, is placed about 15 feet from the slag hole and at such a level as to make it possible completely to drain the hearth.

The walls are about 14 inches thick and 7 feet high and are constructed of the best silica brick. In the front wall of the

furnace are five charging doors through which the raw materials are introduced and repairs to the hearth and walls are made. The doors are lined with fire brick, water cooled, and provided with counterbalances so as to be easily handled. In each door is a small observation hole, or wicket, closed with a metal cover. The back wall of the furnace is closed except for the tapping hole and the slag hole.

The roof of the furnace is arched from front to back as well as from end to end. Its shape is very important, for it serves

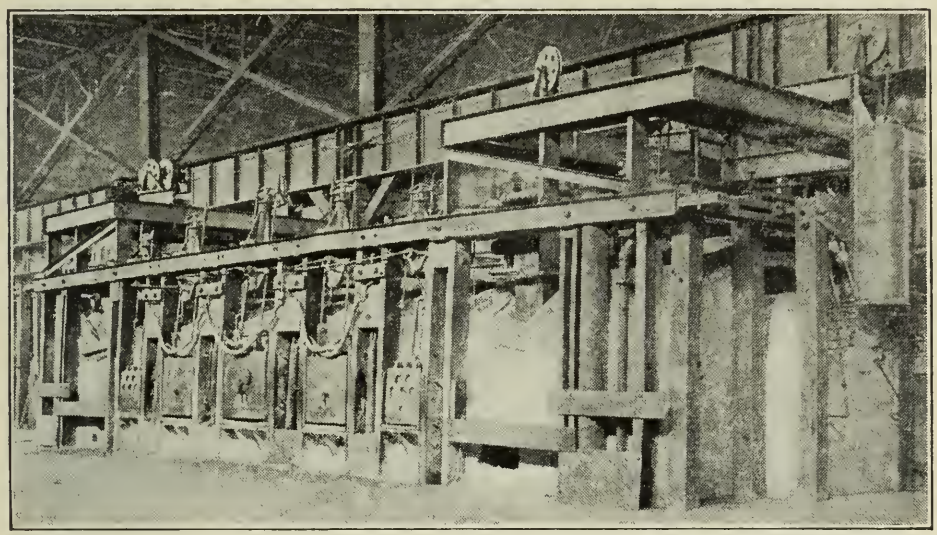

FIG. 187. An open-hearth furnace (charging side)

to reflect the heat down onto the charge on the hearth and directly affects the efficiency of the furnace. This roof is usually about 12 inches thick and is built independent of the side walls. The whole furnace is reënforced with a system of backstraps and I beams. The life of the roof is about 300 heats.

At each end of the furnace are ports for the introduction of the gas and air. There are two ports for air and one for gas, and they are so placed that the air enters above the gas and serves in a measure to protect the roof from the intense temperature of combustion. That this temperature is intense may be judged from the fact that the surface of the silica brick of the roof is in a state of incipient fusion most of the time; they "sweat," as the operator terms it. These ports must be carefully aligned so as to direct the flame down onto the hearth and not against the roof. The life of the furnace depends upon

the life of the ports, for as soon as they are cut away the flame is misdirected and is likely to cut away the roof or walls. They are built of magnesite, chrome, or silica brick, and in many modern plants means are provided for cooling these with air or water in order to reduce corrosion. The bulkheads are the ends of the hearth below the ports.

The air and gas are brought to the furnace through up-and-down-takes at each end. Since these are exposed to a very

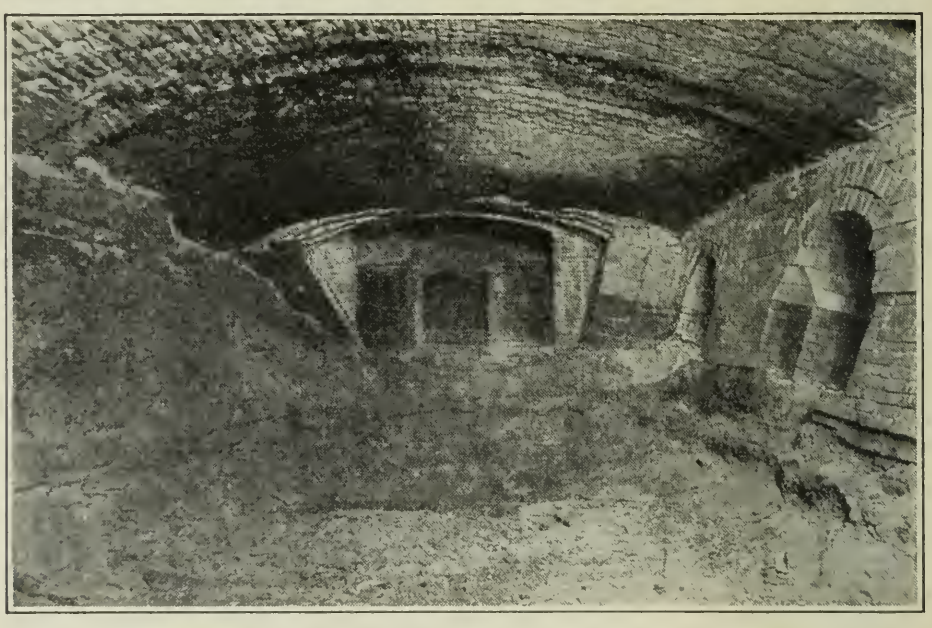

FIG. 188. The interior of an open-hearth furnace

high temperature, they must be constructed of silica brick. These up-and-down-takes are connected with slag pockets for settling out the dust and fine particles of slag, and in turn with the regenerative system for preheating the gas and air.

Producer gas, of course, is used in the furnace described above, but these furnaces are frequently operated on oil, tar, or pulverized coal. It seems an economic crime to burn coal tar in a furnace; but at many plants there is at present no market for the large amounts of tar made in the coking plant, and so it is burned in the furnaces. The total space occupied by the regenerators, which are below the floor level, is from 120 to 150 cubic feet per ton of steel produced. The upkeep of these is no small item in the total cost of producing steel, for their life is seldom more than 600 heats. The fuel consumption

is about 600 pounds of coal (as producer gas), 500 pounds of coal (pulverized), or 45 gallons of coal tar per ton of steel produced.

649. The tilting type. For some special open-hearth processes, such as the Duplex or the Triplex, it is of distinct advantage to employ the tilting, or rolling, furnace. This differs from the ordinary stationary type in that the entire furnace body may be rotated, or tilted, through a considerable angle. This renders the process more flexible, for the contents or any portion of them may be removed at any stage in the process.

There are two types of tilting furnace, known as the Campbell and the Wellman respectively. In the Campbell type the furnace is so constructed that the axis of tilting is coincident with the center of the ports, so that it may be tilted without shutting off the gas or air. Needless to say, this is a distinct advantage. In the Wellman type the ports are not coincident, and the gas and air must be shut off during tilting. Tilting furnaces in general do away with a great deal of the tap-hole troubles, since the tap hole is above the metal and slag lines during most of the cycle. They further enable the operator to drain the furnace bottom thoroughly of all slag and metal. When the furnace is tipped so that the back wall is nearly horizontal, it is much easier to make repairs. Excessive frothing, which gives a great deal of trouble in the simple open hearth, may be avoided by simply tilting the furnace so that slag does not run out through the doors. Both types of tilting furnaces are, however, much more expensive to build and to operate than the simple open hearth.

650. Charging machine. The early furnaces were small and could be charged by hand, but even this was a long, tedious operation. The charging of 125 tons of raw material by such means is out of the question. All this work is now done mechanically with a charging machine. A modern type is shown in Fig. 191. It consists of a heavy truck mounted on a 25-foot track which runs parallel to the front wall of the furnaces. It may serve as many as ten units. On this truck is mounted a second and smaller one with a motion perpendicular to the front wall of the furnace. On the smaller truck is mounted a heavy lever termed a charging arm. This is provided at the outer end with a lug which fits into the socket of the charging boxes. The charging bar can also be revolved so as to invert the box and

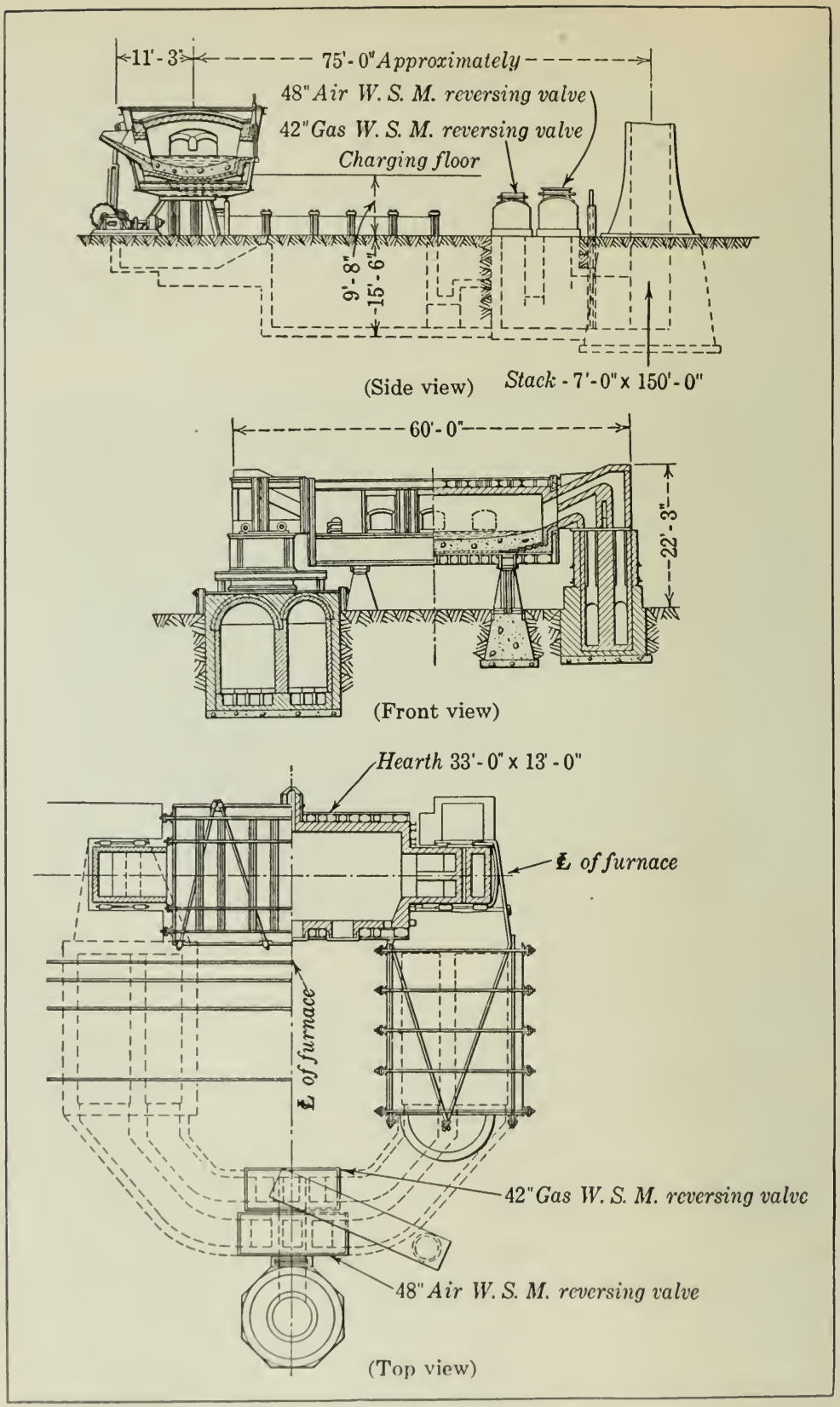

FIG. 189. A 60-ton Wellman tilting open-hearth furnace

empty it. By means of this variety of motions any furnace along the line may be served and the work of charging greatly simplified.

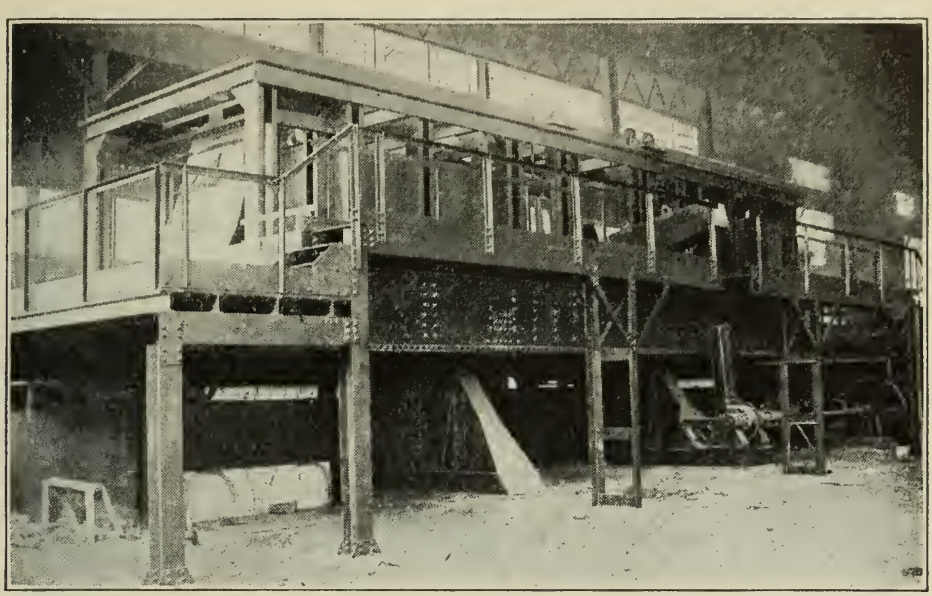

FIG. 190. A 15-ton Wellman tilting open-hearth furnace

In operation the boxes are arranged on trucks in front of the furnace. One box is raised by the arm, thrust into the furnace,

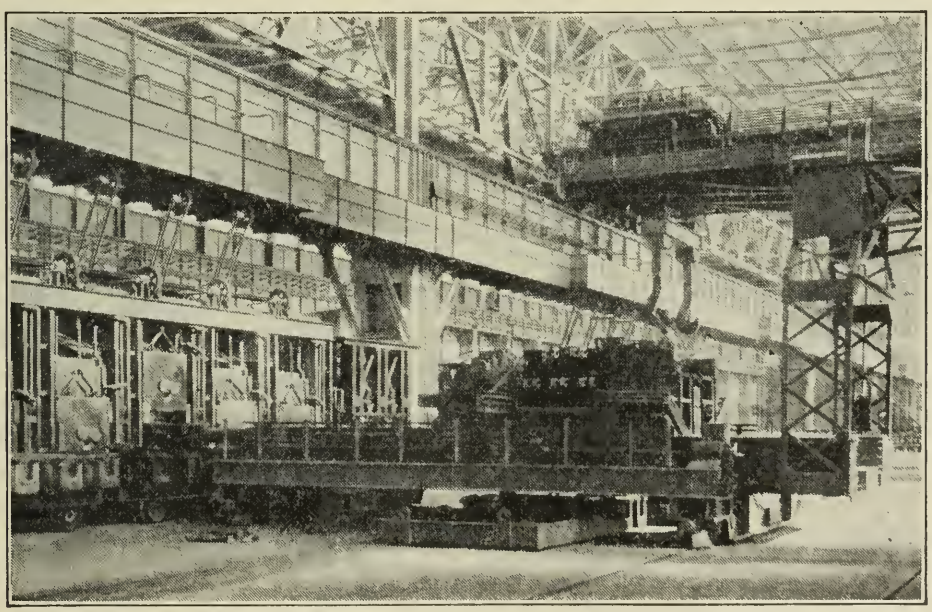

FIG. 191. A charging machine

inverted, and withdrawn. This occupies less than a minute, so that a 100-ton furnace can be charged in less than one hour.

The charging boxes, for handling the raw materials, shown in Fig. 192, are of boiler plate or cast steel. They have a capacity of about 16 cubic feet and will hold a ton of the lightest material used, — limestone. One end of the box has a socket into which fits the T-shaped lug on the end of the charging ram.

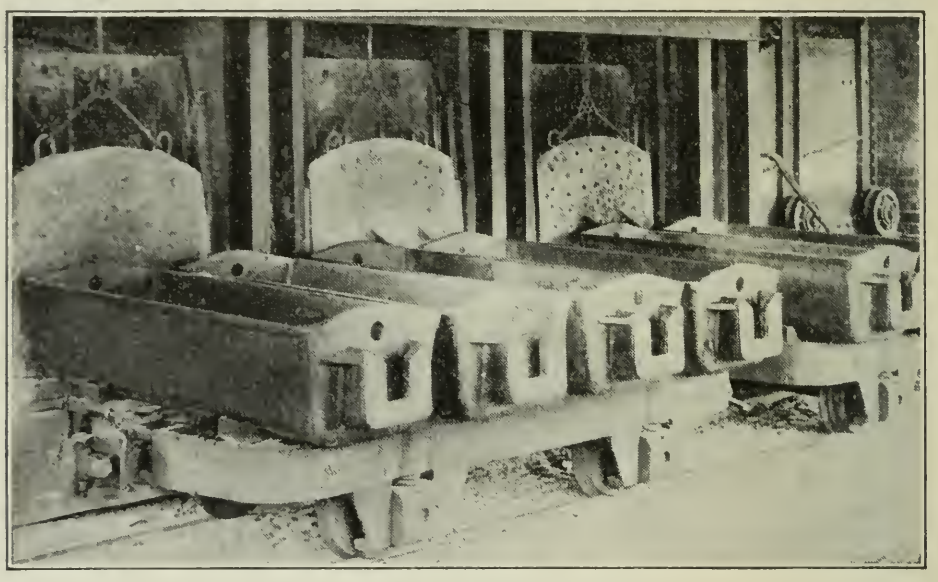

FIG. 192. Charging boxes

651. Other apparatus. The mixers, hot-metal cupolas, stripper, and molds are similar to those used in the Bessemer process. The ladles are much larger, for they must hold all the metal of each heat.

OPERATION OF THE FURNACE

652. Cycle of operations. The preparation of a new bottom is outside the scope of this text; we will assume that the furnace is at heat and ready for the new charge. It can best be divided into five periods: charging and melting, ore boil, lime boil, working period, and tapping.

653. Charging and melting. The raw materials used consist of limestone, ore, scrap, pig iron, and hot metal. The amounts of each will depend entirely upon the chemical composition of the heat and that of the steel to be turned out. It is desirable to have the sulphur as low as possible, for it is not affected to any great extent by the process. The manganese should be fairly high to assist in removing the sulphur, and the silicon low, since

it cuts away the banks. The limestone is always charged first, for the following reasons:

1. In order that it may not be dissolved by the first slag and tapped off.

2. In order not to insulate the top of the charge and thus unduly lengthen the melting period.

3. In order to conserve the lime for the lime boil.

4. In order to make the final slag basic and thus hold the phosphorus in solution.

On top of the limestone is placed the ore, the scrap, and finally the cold pig iron. The gas is then turned on full and the charge begins to melt. Two or three hours is sufficient to bring the charge to a state of complete fusion. Any molten metal is added after the solid constituents have melted.

654. The ore boil. Purification is effected through the oxidation of the various impurities by the iron ore, and through the fluxing, by means of the limestone, of the oxides thus formed. While the purification period has been arbitrarily divided into ore boil, lime boil, and working period, it really starts as soon as the material is charged into the furnace. The oxidation of the manganese and silicon proceeds rather rapidly. Along with the manganese and silicon most of the phosphorus passes into the slag as a phosphate so long as the slag is strongly basic. The carbon is more slowly oxidized to CO, which rises to the surface of the viscous slag, causing it to foam. Just at the close of this period the slag rises almost to the doors. A part of it (the run-off) is usually tapped at this time through the slag hole.

655. The lime boil. As the temperature of the furnace rises the bottom becomes hot enough to effect the calcination of the limestone. Particles of this rise to the surface, and large bubbles of CO_2, quite different from the fine effervescence of CO, rise to the surface of the slag. This agitates the bath and oxidizes the carbon. The temperature must now be raised, for the bath is rapidly losing carbon.

656. The working period. By this time all the impurities except carbon have been eliminated. The operator now adjusts the slag by the addition of lime, iron ore, fluorspar, etc. If it should not be of the proper chemical composition, phosphorus will be reduced and enter the metal, and it will be difficult to adjust the carbon. The temperature of the furnace is gradually

raised, so that when the carbon is at the proper point the furnace will also be at teeming temperature (about 150° C. above the fusion point of the metal). In adjusting the carbon the operator

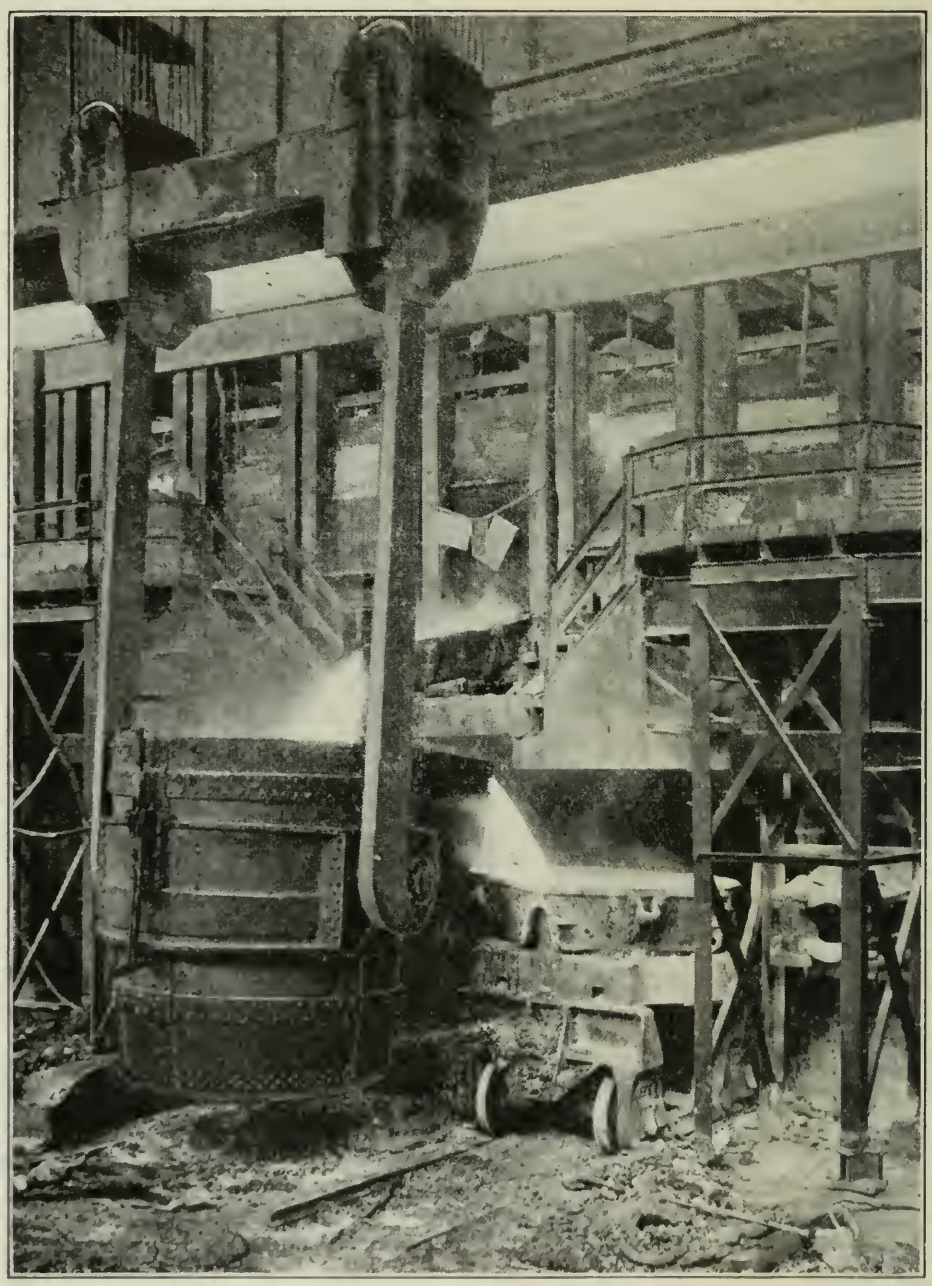

FIG. 193. Tapping an open-hearth furnace

may work the charge down to 0.1 per cent carbon and then recarburize, or he may catch it on the way down. Both methods are in common use. The testing of the bath calls for the highest

skill and long experience, for the carbon content is judged entirely by the appearance of a fresh fracture of a chill specimen.

657. Tapping. When the time comes for tapping, the helper digs out the plug from the tapping hole, knocks out the dolomite which closes the mouth, and allows the charge to run into the ladle. The recarburizers are usually added at this time, before any slag comes from the furnace, in order to promote mixing. The history of the ingot from now on is much the same as in the Bessemer process.

When the furnace has been completely drained, the hearth and the slag line are repaired for the reception of the next charge. Holes in the bottom are repaired with dolomite, and holes which may have formed on the banks or walls are filled with this material to the best of the operator's ability. The tapping hole is sealed with dolomite, and the furnace is ready for charging again. The time from charge to charge is from seven to eleven hours.

Chemistry of the Basic Open-Hearth Process

658. The rôle of FeO. While Fe_2O_3 and Fe_3O_4 are the oxides used, it is the less common oxide FeO which accomplishes the oxidation of the impurities. This is explained by the fact that the first two oxides are stable at temperatures below 1000° C. At higher temperatures, and in the presence of CO_2, Fe_2O_3 is converted into Fe_3O_4 and FeO. The importance of FeO as an oxidizing agent is shown by the following analysis of the first slag formed in the basic open-hearth process:

Table LXXVII. Chemical Composition of Basic Open-Hearth Slag (First)

	Per Cent
FeO	61.0
Fe_2O_3	11.1
SiO_2	8.5
CaO	9.1
MnO	2.3
P_2O_5	0.3
Other oxides	7.7

The rôle of the limestone in the formation of this FeO and the oxidation of the carbon is shown by the following reactions:

$$CaCO_3 = CaO + CO_2.$$
$$CO_2 + Fe = FeO + CO.$$

The order of elimination of the impurities is silicon, manganese, phosphorus, and carbon.

659. Silicon. The oxidation of this impurity is represented by the following reaction:

$$Si + 2\ FeO = SiO_2 + 2\ Fe.$$

The silica thus formed reacts immediately with more FeO of the charge to form a slag, thus,

$$3\ SiO_2 + 2\ FeO = (FeO)_2(SiO_2)_3,$$

which rises to the surface and covers the molten iron. A great deal of the iron in the initial slag is replaced by the calcium and magnesium of the charge, thus:

$$(FeO)_2 \cdot SiO_2 + 2\ CaO = (CaO)_2 \cdot SiO_2 + 2\ FeO.$$

The following analysis is of the slag ready to tap (contrast this with the analysis in Table LXXVII):

TABLE LXXVIII. BASIC OPEN-HEARTH SLAG READY TO TAP

	PER CENT
SiO_2	10.80
FeO	22.01
Al_2O_3	1.55
P_2O_5	5.61
MnO	9.00
CaO	44.00
MgO	6.53

660. Manganese. Most of the silicon is oxidized before any manganese is eliminated, because silicon can reduce manganese from the slag. The oxidation of the manganese then proceeds according to the following reaction:

$$Mn + FeO = MnO + Fe.$$

The MnO is then slagged by the silica already formed. Some manganese is later liberated by reactions with CaO and MgO. If the manganese content is fairly high, MnS is formed and enters the slag, eliminating a part of the sulphur in this way.

661. Phosphorus. This impurity is removed according to the following reaction:

$$2\ Fe_3P + 8\ FeO = (FeO)_3 \cdot P_2O_5 + 11\ Fe.$$

In order that this may go on, the slag must be very basic and slightly oxidizing. Furthermore, no silicon can be present, for it has the power of reducing phosphorus from the phosphate. It is for this reason that the acid Bessemer process has no effect upon the phosphorus. With so much free silica present the P_2O_5 is thrown out of the slag, and the phosphorus is reduced at this high temperature by the silicon or carbon.

662. Carbon. The carbon is eliminated according to the following reactions,

$$C + FeO = CO + Fe.$$
$$Fe_3C + FeO = CO + 4\ Fe.$$

It is the tiny globules of CO rising through the slag that give it the characteristic frothy appearance of the ore boil.

663. Sulphur. There is very little elimination of this element in the open-hearth process. At the low temperatures employed in nonferrous roasting the sulphur is easily oxidized and escapes as SO_2, but at the high temperature of the basic open-hearth furnace the CO tends to reduce this SO_2. Besides, there is an increased tendency for the iron to unite with the sulphur at these elevated temperatures. As a matter of fact, there is very likely to be an increase in the sulphur content of the metal, owing to absorption from the furnace gases, particularly when using fuels high in this troublesome element.

THE ACID OPEN-HEARTH PROCESS

664. General. This process is like the basic open-hearth process except that the hearth is made up of siliceous instead of basic material. Because of the acidic character of the lining and slag, there is no elimination of phosphorus or sulphur; so the raw materials used must be low in these impurities.

665. The furnace. In general details, such as hearth, ports, roof, regenerators, etc., the acid furnace is the same as the basic one already described. The bottom only is made up in a different manner. Pieces of sandstone or gravel about 2 inches in diameter are scattered over the bottom of the furnace, and the furnace temperature is raised until these just begin to fuse. A layer of silica sand about $\frac{1}{4}$ inch thick is then spread over this and fused into place. When this is well glazed, another layer of sand is added until a bottom from 12 to 20 inches in

thickness has been built up. The sand used for this purpose must contain not less than 95 per cent of SiO_2 and very little CaO, MgO, or FeO.

Operation

666. Cycle of operations. The acid process is somewhat simpler than the basic; for since the silicon and manganese are eliminated almost immediately, the heat is worked for carbon alone. It may be divided, for the purposes of this discussion, into four periods: charging, melting, working, and tapping.

667. Charging and melting. The raw materials are largely scrap and pig iron. The proportion of each used may vary between wide limits according to local market conditions and the kind of steel being produced. Iron ore and limestone may be added after the charge is melted, but not with the solid materials, or they would tend to flux the hearth. The scrap and pig iron must contain slightly less phosphorus and sulphur than the finished steel, for, owing to the elimination of silicon and manganese and the loss of iron, there is a slight increase in the percentage of these elements in the finished steel. For most acid work, in order to get a fast-working charge and reduce hearth repairs, the operator likes to get pig iron of about the following composition:

Si	Less than 2 per cent
Mn	From 1 to 2 per cent
P	Under 0.08 per cent
S	Under 0.04 per cent

In the larger furnaces the charging is carried out with a machine; in the smaller ones it is done by hand. Often, in foundry work, furnaces as small as 10 tons capacity are used. The lighter scrap is usually charged first, in order to protect the hearth from the fall of the heavier pieces. The gas current is reversed every ten to fifteen minutes, and the temperature raised rapidly in order to melt the charge as soon as possible. At the end of about five hours the contents will be completely melted. The operator then adjusts his slag to the proper composition by adding lime, iron ore, or silica sand as conditions require. Care must be exercised in adding the first two reagents, in order not to corrode the banks or the hearth. The chemical composition of two acid slags is given (in per cents) in Table LXXIX.

TABLE LXXIX. ACID OPEN-HEARTH SLAGS

HEAT	SiO_2	FeO	MnO	P_2O_5	Al_2O_3	CaO	MgO
	Per Cent	*Per Cent*	*Per Cent*	*Per Cent*	*Per Cent*	*Per Cent*	*Per Cent*
No. 1	52.06	20.38	20.52	0.035	3.07	4.35	Trace
No. 2	55.60	28.90	10.23	0.022	4.16	0.70	0.12

668. Working. With a slag of the proper composition the operator now proceeds to lower the carbon content. He must also maintain the temperature of the furnace at the proper point, so that when the carbon content has reached the desired figure the contents of the furnace will be at teeming temperature. Chill samples are taken every few minutes, and if these show that the carbon is being eliminated too slowly a little iron ore is added. The working period covers from three to four hours, and, as in the basic process, the heat may be caught on the way down or recarburized to the desired carbon content. It is inadvisable to add very much ore during the last part of the working period, as the steel will dissolve oxide.

669. Tapping. When the heat contains the correct amount of carbon and is thoroughly deoxidized and at the proper teeming temperature, the tapping hole is burned out and the charge allowed to run into the ladle. The necessary recarburizer is added before the slag begins to flow. The furnace is then cleaned out and made ready for the next charge.

CHEMISTRY OF THE ACID PROCESS

670. Chemistry. Only the silicon, manganese, and carbon are affected by this process. The phosphorus and sulphur, because of the acidic character of the slag, remain unaffected.

671. Silicon and manganese. Practically all the silicon and manganese are removed in the early stages of melting. Since no iron ore has been added, the only oxidizing agents available are oxygen, water vapor, and carbon dioxide. The reactions involved are probably as follows:

$$3\,Fe + 2\,O_2 = Fe_3O_4.$$
$$3\,Fe + 4\,H_2O = Fe_3O_4 + 4\,H_2.$$
$$Fe + H_2O = FeO + H_2.$$
$$Fe + CO_2 = FeO + CO.$$

The iron oxides thus formed in the melting of the charge then become available as oxidizers of the manganese and silicon, thus:

$$Si + 2\ Fe_3O_4 = SiO_2 + 6\ FeO.$$
$$Si + 2\ FeO = SiO_2 + 2\ Fe.$$
$$Mn + Fe_3O_4 = MnO + 3\ FeO.$$
$$Mn + FeO = MnO + Fe.$$

The MnO and SiO_2 form slags, thus:

$$3\ SiO_2 + 2\ FeO = (FeO)_2 \cdot (SiO_2)_3.$$
$$MnO + SiO_2 = MnO \cdot SiO_2.$$

672. Carbon. A small amount of carbon is eliminated during the melting, but most of it is removed during the carbon boil. Since the oxidation of manganese and silicon and the formation of the slag have used up most of the iron oxide, it becomes necessary to add more in the form of iron ore. This is done very carefully in order not to slag the banks of the hearth. The temperature is also raised in order that the following reactions may go on:

$$4\ C + Fe_3O_4 = 4\ CO + 3\ Fe.$$
$$C + FeO = CO + Fe.$$

The escape of the CO gas causes a violent ebullition as in the basic process.

673. Open-hearth versus Bessemer. The Bessemer process has been fighting a losing battle for a number of years against the open-hearth process. Statistics bear this out, as shown in Table LXXVI. The reasons for this are as follows:

1. The Bessemer requires about twelve minutes; the open-hearth, nine hours. During this longer period a great deal more attention and care can be given to the purification. Even under the best of conditions Bessemer steel contains more oxygen than open-hearth steel, and if the blow is continued just a few seconds too long, the steel may be completely ruined.

2. In making Bessemer steel we must start with pig iron containing less than 0.09 per cent of phosphorus. Ores from which material of this grade can be made are very scarce in this country and command a premium on the market.

3. In the Bessemer process the heating of the charge is accomplished entirely by the oxidation of the impurities. There is, therefore, the danger of overheating the metal or of having

it too cool. In the open-hearth process, on the other hand, heat can be supplied at any rate and the bath be under complete control at all times.

4. In the open-hearth process we can stop decarburization at any point and add only a small quantity of recarburizer. This small quantity can be mixed with the steel better than a large quantity. In the Bessemer process we must get rid of practically all the carbon and then add a relatively large amount of recarburizer.

There are certain fields, however, in which Bessemer steel does, and perhaps always will, enjoy popularity. For example, very low-carbon steel such as is used in the making of wire and welded pipe can be made more cheaply by the Bessemer process. Similarly, Bessemer steel is often used for tin plate and sheet work, since the small amount of phosphorus left behind is an advantage in preventing the sheets from sticking together. Certain rolling-mill operations in which a small amount of metal at frequent intervals is desired can adapt themselves to Bessemer operation better than to open-hearth.

THE DUPLEX PROCESS

674. General. We have described the relative advantages and disadvantages of the open-hearth and Bessemer processes. In an effort to combine the two into a more nearly ideal process the Duplex process was devised. Briefly, it consists of blowing the molten iron in an acid Bessemer converter until the silicon, manganese, and a part of the carbon are removed. While still molten the charge is transferred to a basic open-hearth furnace, and the phosphorus and the remainder of the carbon are removed in the usual way. This method has many advantages, among them the following:

1. Shortening of the open-hearth operation so that the operator gets 40 heats per week as against only 15 per week in the straight open-hearth.

2. It renders the operator independent of the scrap market, for he can make his own scrap, so to speak, in the converter.

3. The elimination of some of the impurities in the converter saves fuel and greatly prolongs the life of the open-hearth furnace.

The chief objections to the process are the following:

1. It requires two separate plants, the maintenance of which, in dull times, may cost many times the saving made at full tonnage.

2. The double conversion cost and extra handling of the molten metal result in increased oxidation of the iron.

675. The Talbot furnace. The process is usually carried out in a tilting furnace. The hearth is usually deeper than in the ordinary open-hearth, for it must hold up to 200 tons of charge. In general two methods of duplexing are in common use. In one the carbon is only partly eliminated in the Bessemer, and is then removed, together with the phosphorus, in the open-hearth. In the other method the charge is blown in a Bessemer converter until practically all the carbon is removed and the metal really represents a high-phosphorus steel which can then be purified in the basic open-hearth.

676. Operation. In order to make the process as flexible as possible and allow for repairs, it is carried out with three 20-ton Bessemer converters and three 200-ton Talbot furnaces. Whenever possible the campaign extends from week-end to week-end, all repairs being made after midnight on Saturday.

Let us assume that the furnace has been cleaned and repaired and is at heat ready for charging. The slag is made ready by melting down 8000 pounds of limestone and 2000 of roll scale. This is repeated until a bath of about 50,000 pounds of slag has been prepared. The success of the whole process depends upon the proper adjustment of this slag. Two Bessemer heats of about 40,000 pounds each are then transferred to the furnace, being poured in, while still molten, through runners or launders. The first ladle is blown to about 0.60 per cent carbon; the second is a ladle of "soft" metal with about 0.06 per cent of carbon. Then a vigorous boil is induced in the charge by adding another "kicker," or ladle, of 1.5 per cent carbon metal. The metal is poured through the slag, and at the high temperature maintained, and with such intimate mixing, the phosphorus is oxidized almost immediately. Alternate "soft" and "kicker" ladles are then added, as the carbon content of the charge indicates, until a bath of about 200 tons has been prepared. The slag is then adjusted and the charge worked down in the usual way.

Table LXXX. Analysis of Talbot Slag

	Per Cent
SiO_2	6.4
FeO	21.7
Fe_2O_3	6.9
Mn	1.1
P	3.3
CaO	44.0
MgO	8.0
Other oxides	8.6

Note that the slag given in Table LXXX is very basic and highly oxidizing, in order to hold the phosphorus in solution.

The tap hole is then opened and plugged with a piece of wet sacking, and the furnace is tilted forward for pouring. Before the sack is burned out and the hole clear, the slag has risen above the tapping hole and only clear metal comes out. This is recarburized and deoxidized in the usual way.

About 100 tons of metal is taken from the furnace before it is tilted back to the working position. Lime and roll scale are added to replace the slag lost in the tapping and to bring it up to the proper chemical composition. Alternate "soft" and "kicker" ladles are then added until the furnace is full again. The latter gives a violent reaction, and the slag usually overflows through the slag notch in the front of the furnace. If the ebullition becomes too violent, with the attendant danger of excessive loss of metal, the furnace can be tilted back. The average time from tap to tap is about three hours. Contrast this with the nine-hour campaign on the straight open-hearth process. At the end of the week the furnace is drained and the repairs made which are necessary in order to get it ready for the next campaign.

677. Triplex process. This process, a modification of the Duplex, is used on very high-phosphorus pig iron (over 0.8 per cent). Since there is but little of this material made in this country, the process is not in common use. With such high-phosphorus metal the slag becomes very rich in P_2O_5. Some of this slag is unavoidably drawn off in the ladle during tapping, and the recarburizers reduce some of the phosphorus. To overcome this difficulty two open-hearth furnaces are employed. In the first the major portion of the phosphorus is taken out in the

form of a high-phosphorus slag which commands a ready market in the fertilizer industry. The charge is then taken to a second open-hearth furnace, where the metal is finished beneath a new low-phosphorus slag. It could be done by changing slags in the same furnace, but such a method is long and cumbersome. Naturally the process is more costly than the Duplex.

ELECTRIC FURNACES

678. General. It has been pointed out that crucible steel is superior to either open-hearth or Bessemer, largely because it is free from gases and solid inclusions. The crucible furnace, however, is cumbersome, and the process is expensive, owing to the small tonnage handled and the large amount of hand labor necessary. Electric furnaces offer the same or better melting conditions on a much larger scale. Metallurgists have welcomed this type of furnace for the following reasons:

1. The heat can be easily regulated and maintained.
2. A very high temperature is possible.
3. An oxidizing, reducing, or neutral atmosphere can be maintained at will.
4. Changes in temperature can be made quickly.
5. It introduces no foreign elements into the metal (such as sulphur from the combustion of the fuel).

It is not surprising, therefore, that the manufacture of electric steel has made rapid strides in the last few years, as indicated by Table LXXXI.

TABLE LXXXI. PRODUCTION OF ELECTRIC STEEL IN THE UNITED STATES (IN TONS OF 2240 POUNDS)*

YEAR	INGOTS	CASTINGS	TOTAL
1910	50,821	1,320	52,141
1915	46,348	23,064	69,412
1920	346,956	155,196	502,152
1921	84,404	85,095	169,499
1922	191,057	154,982	346,039
1923	279,914	235,958	515,872
1924	225,977	206,549	432,526
1925	335,978	279,534	615,512
1926	325,278	326,445	651,723
1927	371,278	294,809	666,087

* Mineral Industry.

679. Héroult electric furnace. A modern 7-ton Héroult furnace is shown in Fig. 194. At present these furnaces are being manufactured in units as large as 60 tons capacity. It resembles somewhat a tilting open-hearth furnace, consisting of a circular

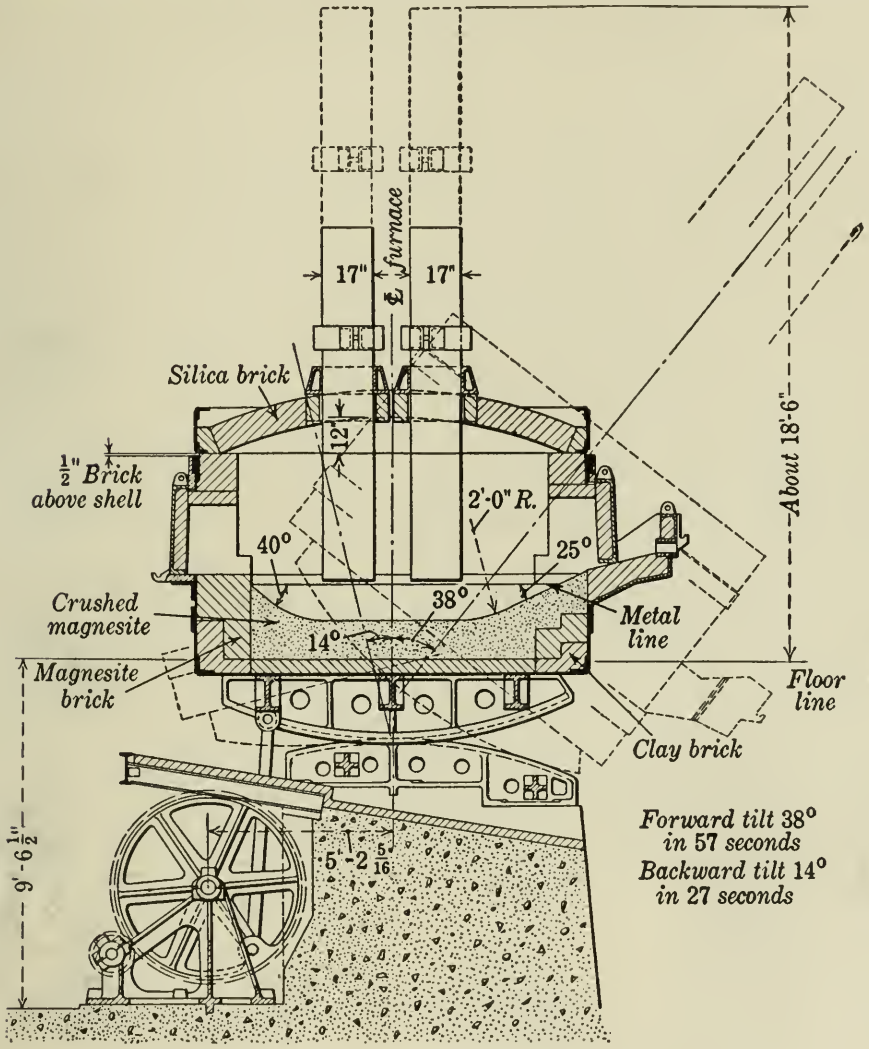

FIG. 194. A Héroult electric furnace

steel-plate shell with a rounded bottom. By means of an electrically operated tilting mechanism the furnace can be tilted forward 38 degrees for discharging or tilted back 14 degrees for charging. The bottom is built up of clay brick, magnesite brick, and grain magnesite to a total thickness of about 18 inches. The roof is lined with 9 inches of silica brick and is removable. It is pierced with three openings for the carbon electrodes. These electrodes, from 4 to 24 inches in diameter, depending upon

the size of the furnace, are held in electrically controlled, automatic electrode holders. They may also be operated manually by means of a hand wheel. The source of current (3-phase) is

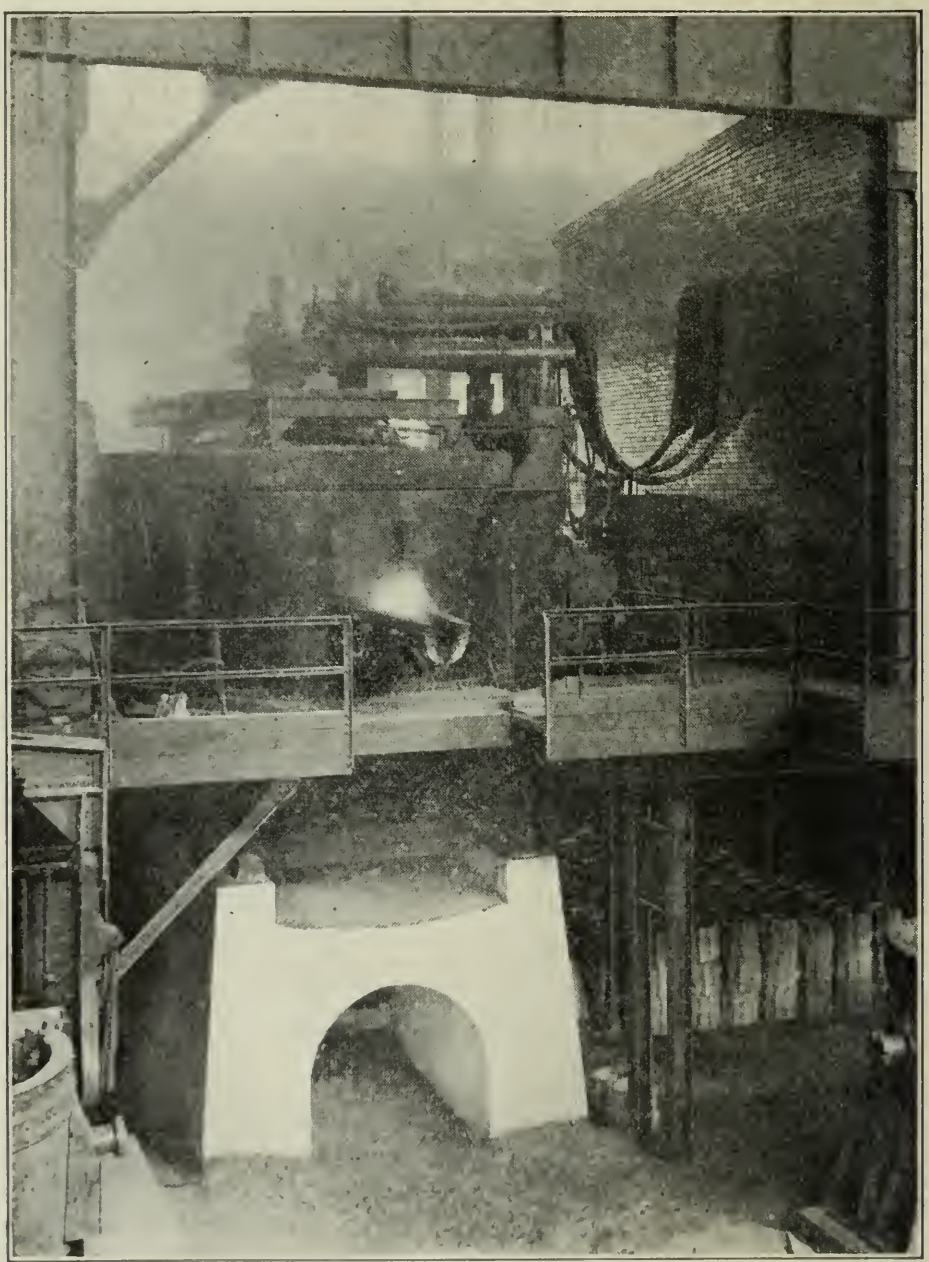

FIG. 195. A 25-ton Héroult electric furnace

a transformer, to give 150 volts, full capacity, or, with reduced capacity, taps for 135, 120, 105, and 90 volts. The arcs are maintained between the electrodes and the metal bath. There

are copper cooling chambers surrounding the electrodes where they enter the roof. Water circulating through these keeps the carbon electrodes within permissible temperature limits. The electrode holders are also water-cooled.

In charging the furnace the electrodes are raised to their highest position so that the scrap may be thrown in. When charged, two of the electrodes are lowered, by hand, until an arc is established. The other is then lowered and adjusted. During the melting period, owing to changes in the cold scrap, the electrodes must be carefully watched and usually adjusted by hand, but after a bath of molten metal is formed automatic control is easy. When the heat is finished, the electrodes are raised, the current switched off, and the furnace tilted for tapping.

Operation

680. Cycle of operations. The campaign of a charge may be divided into the following periods: charging, deoxidizing and finishing, and tapping.

681. Charging. For scrap heats the material is added to the furnace through a chute, the coarser material on the bottom. If molten metal direct from the open-hearth or Bessemer is used, it is poured into the furnace from a ladle. Since the specifications are usually close, a sample is taken for chemical analysis. If high-carbon steel is being made from low-carbon stock, anthracite is added at this time and the current is turned on.

682. Deoxidizing and finishing. As soon as the contents of the furnace have reached a state of fusion, the slag mixture of lime, coke dust, and fluorspar is made up. A sample is then taken, and further additions are made to the slag or metal, as these analyses indicate. The analysis of a typical slag is given (in per cents) in Table LXXXII.

Table LXXXII. Final Electric-Furnace Slags*

Heat	SiO_2	Fe	CaO	MgO	Mn	S	CaC_2	Al_2O_3
	Per Cent	*Per Cent*	*Per Cent*	*Per Cent*	*Per Cent*	*Per Cent*	*Per Cent*	*Per Cent*
No. 1	18.40	0.32	61.26	7.27	0.35	1.30	0.46	5.95
No. 2	20.48	0.72	61.82	8.40	0.60	0.80	0.19	3.61

* The Making and Shaping of Steel. Carnegie Steel Company.

When, in the judgment of the operator, deoxidation is complete and the amount of carbon, silicon, and manganese is determined, solid alloys are added to bring the steel up to the required composition. A simple test to indicate complete deoxidation is as follows: The operator takes a small sample of slag in a ladle and pours it into water. If deoxidation is complete, there will be a strong odor of acetylene. The addition of the ferrous alloys chills the furnace; so it is next brought up to teeming temperature and the contents made ready for tapping.

683. Tapping. Precautions are taken, in tapping and teeming, not to include any slag in the metal. In order to show better the history of an electric heat, Table LXXXIII is given to illustrate the schedule of operations in a low-carbon-alloy heat.

TABLE LXXXIII. A LOW-CARBON-ALLOY HEAT

Molten charge as finished at open hearth: C = 0.09%; Mn = 0.34%; P = 0.015%; S = 0.034%.

Order: C = 0.12–0.20%; Mn = 0.40–0.70%; P = under 0.040%; S = under 0.040%; Si = under 0.20%; Cr = 0.40–0.80%; Ni = 1.00–1.75%.

TIME	ADDITIONS
10.55	Charge, 50,800 lb. Test: C = 0.08%; Mn = 0.29%; P = 0.010%; S = 0.042%.
11.15	Power on.
12.00	First slag mixture: lime, 500 lb.; fluorspar, 150 lb.
12.30	¾ second slag mixture: lime, 750 lb.; fluorspar, 125 lb.; coke dust, 100 lb.; sand, 100 lb.
12.45	Chemical analysis { front door: C = 0.08%; Mn = 0.24%. side door: C = 0.08%; Mn = 0.22%.
12.50	200 lb. ferromanganese (Mn = 78%).
12.55	446 lb. ferrochrome (Cr = 70%).
1.00	730 lb. nickel (Ni = 99%).
1.30	½ third slag mixture: lime, 50 lb.; coke dust, 75 lb.
1.45	½ third slag mixture.
1.50	30 lb. ferromanganese and 60 lb. 50% ferrosilicon.
2.00	Heat tapped.

Final analysis: C = 0.20%; Mn = 0.51%; P = 0.009%; S = 0.028%; Si = 0.03%; Cr = 0.54%; Ni = 1.28%.

CHEMISTRY OF THE ELECTRIC PROCESS

684. Elimination of impurities. Very little elimination of impurities is effected in the electric furnace; these must all be removed by some previous process or else not be present in the

scrap being melted. The chief changes brought about are deoxidation and desulphurization.

685. Deoxidation. If molten metal is being used, a little manganese is purposely left in the metal; if scrap is being used, material with the proper manganese content is purchased. This manganese serves to remove a part of the dissolved oxygen, thus:

$$FeO + Mn = MnO + Fe.$$

This MnO then comes in contact with the carbon of the charge and reacts thus:

$$MnO + C = Mn + CO.$$

The CO escapes and the manganese returns to the steel and may be used again for deoxidation.

686. Desulphurization. The temperatures employed in the electric furnace are much higher, particularly near the electrodes, than in the open-hearth furnace. At this high temperature calcium carbide is formed, thus:

$$CaO + 3\ C = CaC_2 + CO.$$

This carbide then reacts to form a sulphide which is insoluble in the iron and is thus eliminated:

$$3\ FeS + 2\ CaO + CaC_2 = 3\ Fe + 3\ CaS + 2\ CO.$$

A similar elimination may be effected with carbon, thus:

$$FeS + CaO + C = Fe + CaS + CO.$$

There must be no metallic oxides in the slag, or the following reaction,

$$CaS + FeO = FeS + CaO,$$

would take place and throw the sulphur back into the steel. Calcium carbide would react thus,

$$CaC_2 + 3\ FeO = 3\ Fe + CaO + 2\ CO.$$

So the odor of acetylene in the slag tests indicates the presence of carbide, which in turn indicates complete deoxidation.

687. Advantages of the electric process. The electric furnace is undoubtedly the most satisfactory one from a metallurgical standpoint, for the following reasons:

1. No impurities are introduced into the metal.
2. The alloying reagents can be introduced while the steel is still in the furnace.

3. The tonnage treated by each furnace is much larger than in the crucible process.

4. Electric steel is more likely to be free from segregations, inclusions, and gas.

5. Electric steel is more ductile at low temperatures than that made by any other process.

6. Higher temperatures can be reached and maintained.

7. Desulphurization and deoxidation can be carried out at the same time.

8. The loss of metal is less than in any other refining process.

THE EFFECT OF IMPURITIES ON STEEL

688. General. The steel of commerce is a very complex mixture of a number of elements besides iron, — complex not only because there are sometimes as many as eight elements present, but also because some of these may exist in more than one form or combination. Carbon, for example, may occur in the steel as plain graphite, as temper carbon, or as cementite (Fe_3C). Each of these different forms confers entirely different properties upon the steel. The alloy steels are treated in another chapter; so the only impurities to be discussed here will be those commonly found in simple steel, — that is, carbon, manganese, silicon, phosphorus, and sulphur.

689. Carbon. Carbon is beyond question the most important element in plain carbon steel, — so much so that the ordinary nomenclature is based on the percentage of this element in the steel. It may be present up to 4.50 per cent, but the useful steels range from 0.02 to 1.50 per cent carbon. This carbon may occur combined (as Fe_3C), or uncombined (as graphite or temper carbon), or as a mixture of these. The most important effect of this element is upon the hardness, strength, and ductility of the metal. In the case of *naturally cooled* steel the average of a great number of tests indicates that for each 0.1 per cent of carbon added, up to a maximum of 0.9 per cent, these properties are affected as follows:

Yield point is raised 3987 pounds per square inch.
Tensile strength is raised 9363 pounds per square inch.
Elongation is reduced 4.33 per cent.
Reduction in area is reduced 7.27 per cent.

These figures may be applied only to plain carbon steel which has been fully annealed. Above 0.9 per cent carbon the steel becomes very hard and brittle and follows no fixed rule.

690. Manganese. Next to carbon this is probably the most important element in plain carbon steel. The amount may vary from almost nothing up to 2 per cent. The alloy steels may contain as much as 14 per cent. If there is enough manganese it will combine with the sulphur to form manganese sulphide, which is soluble in steel and does not have the deleterious effects of the iron sulphide. If there is more than enough to combine with the sulphur, the remainder combines with the carbon to form Mn_3C. This acts similarly to iron carbide. The chief use of Mn is as a deoxidizing and desulphurizing agent. Manganese in excess of that required for these purposes tends to increase the tensile strength and to cause the material to roll and forge better.

691. Silicon. The silicon in plain carbon steel varies from 0.50 to 4 per cent. It combines with the iron to form a silicide (FeSi) and dissolves in the steel to form a solid solution. It is used in steel mainly for its degasifying and deoxidizing effect. Up to a maximum of 0.7 per cent silicon is beneficial. Up to that limit it appears to increase the tensile strength as well as the resistance to shock and fatigue. In casting it tends to prevent blowholes. It retards the absorption of carbon in case-hardening. It acts somewhat like phosphorus in preventing thin sheets from sticking together during the rolling process.

692. Phosphorus. Phosphorus occurs in the iron ores as the phosphate. Practically all of this is reduced in the blast furnace and enters the pig iron as the phosphide (Fe_3P). Phosphorus is considered a harmful impurity in steel and iron, since it makes the material brittle and lowers its resistance to shock. It has but one advantage, — that of conferring increased fluidity on cast iron. In irons the phosphorus content will range from 0.02 to 0.8 per cent; in steels it ranges from 0.03 to 0.13 per cent, with 0.04 as the most common figure.

693. Sulphur. This is probably the most harmful impurity in steel or iron. It is likewise the most difficult one to remove. It enters the blast furnace with the coke or iron ore. It is possible, under proper furnace conditions, to remove most of this sulphur in the blast furnace, but ordinarily at least half

of it enters the iron as FeS, forming a eutectic with the iron. This iron sulphide causes hot-shortness in the steel. It probably accelerates corrosion as well. The element is not so black as formerly painted, for recent investigations have shown that as much as 0.06 per cent of sulphur, with a sufficient excess of manganese, may not harm the steel. The quantity of sulphur in iron ranges from 0.015 to 0.150 per cent, with an average of about 0.050; in steels it is usually kept below 0.040 per cent. Sulphur promotes machinability, so that in screw stock the sulphur content may rise as high as 0.130 per cent.

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CHAPTER XVI

METALLOGRAPHY

694. Definition. Metallography may be defined as the study of the internal structure of metals and alloys and its relation to their composition and to their physical and mechanical properties, and of their industrial and scientific application.

695. Crystallization. It is now generally recognized that all metals and alloys are crystalline substances. In passing from the liquid to the solid state the atoms or molecules arrange themselves so as to form regular geometric solids like the hexagonal prism, the cube, or the octahedron. In a piece of slowly cooled antimony the crystals are visible to the naked eye; in some quenched steels the highest magnifications of our microscopes fail to render the crystals visible, but X-ray examination proves that even this fine-grained metal is crystalline.

It is a familiar fact that sodium chloride can be dissolved in water. Such a solution has all the physical properties of water, and if it were not for the taste and certain chemical tests we should not know that the salt was there. Microscopic examination fails to show its presence. The salt has been changed from the relatively large crystals in which it exists in the common article of commerce to a molecular dispersion in the water. If a part of the water is removed by evaporation, and the solution is cooled, crystallization begins; that is, the salt tends to change back into the coarser form. Where there is freedom of growth, more or less perfect crystals of pure NaCl separate out of the liquid. There may be one large crystal of the pure salt or a number of minute ones, depending upon solution conditions, but every one of these will be in the form of a cube. When there is not freedom of growth, one crystal being in contact with another, the form of each is modified to meet this new set of conditions. Similar crystals of the salt will form an igneous solution, but since solidification in this case takes place in a vessel and a viscous liquid, not in a mobile

medium like water, the individual crystals are not visible to the naked eye.

Now take a pure metal and study the mechanism of crystal growth. A polished and etched surface of such a metal will appear under the microscope as shown in Fig. 215 (p. 515). That is, it will consist of a number of roughly polygonal figures. They may be of approximately the same size, but there seems to be no resemblance to the regular geometric figures assumed by salt, alum, copper sulphate, etc. in crystallization. This does not appear to satisfy the conditions of crystal growth just outlined. Rosenhain's classic exposition* of this crystal growth is illustrated in Fig. 196. Let us assume that the metal has just begun to crystallize from the molten state, and that this crystallization proceeds from a number of centers, as indicated in *a*. As the melt cools, perfect crystals attach themselves to those already formed, and by successive stages the grains grow, as indicated in *b*, *c*, *d*, *e*, and *f*, until they meet. We are able to show the growth in but one plane; actually it takes place in three dimensions.

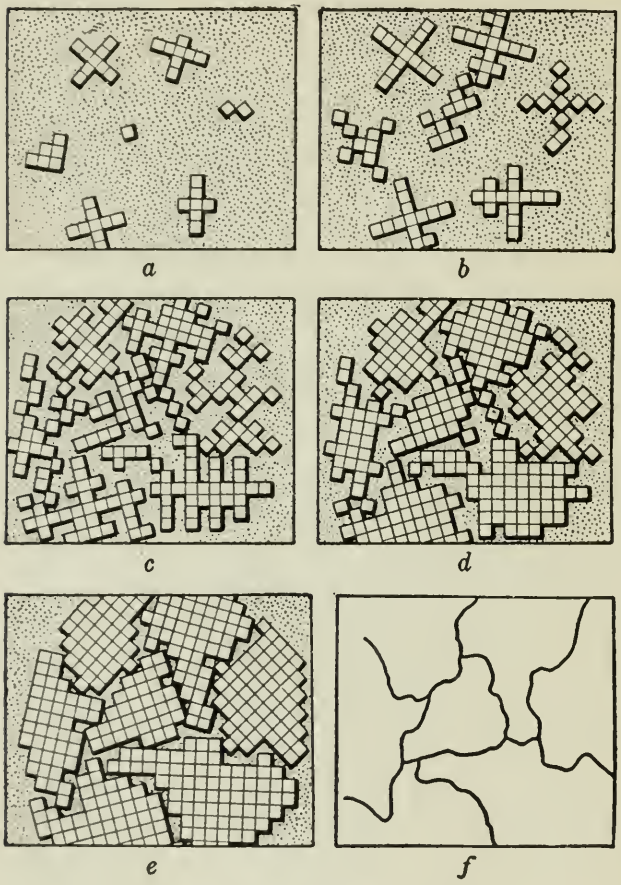

FIG. 196. Crystal growth

After Rosenhain

696. Atomic structure. It has further been determined by X-ray analysis that all metals have a certain regular arrangement of the atoms. They are not mixed in a disorderly fashion.

* Walter Rosenhain, Introduction to Physical Metallurgy.

In addition, it has been proved that the atoms of copper, for example, always arrange themselves in the same definite geometrical pattern, never in any other, so far as we have been able to determine. This pattern constitutes what is known as a space lattice and consists of a series of points so located in space that each point is situated similarly to every other point. We can then divide the space lattice into unit cells by three sets of parallel planes, as indicated in Fig. 197. The planes of each set will be parallel and equidistant from each other. Planes passed through different sets may intersect at any angle. The lines of intersection of these planes is what is known as the space lattice.

Practically all metals crystallize in either one of two modifications of the cubic system, — the body-centered space lattice

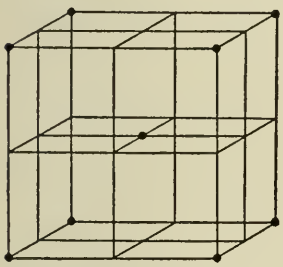

FIG. 197. Body-centered lattice

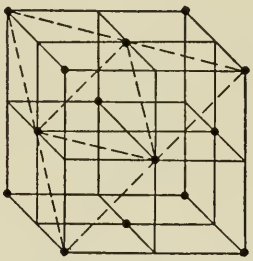

FIG. 198. Face-centered lattice

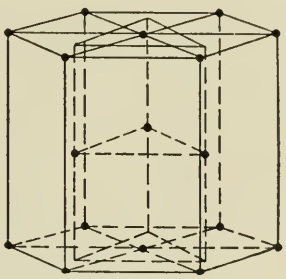

FIG. 199. Hexagonal close-packed lattice

or the face-centered space lattice. The former is shown in Fig. 197, and the latter in Fig. 198. In the body-centered lattice there is an atom at each of the eight corners of the cube and one atom at the center. In the face-centered lattice there is one atom at each of the eight corners of the cube and one in the center of each of the six faces. Another and less common structure is the "close-packed hexagonal" shown in Fig. 199; in this arrangement there is an atom at each of the prism corners and one at alternate prism centers. In these ideal sketches the dots really represent atom centers; the atoms themselves are closely packed and held together by tremendous attractive forces.

All malleable and ductile metals, such as copper, aluminum, gold, nickel, and gamma iron, have face-centered lattices (differing only in the distance between corresponding atoms). The best electrical conductors and heat conductors have the same arrangement. Both ductile and brittle metals are found in the body-centered and close-packed hexagonal arrangement.

697. Orientation. By orientation is meant the arrangement of the principal crystallographic planes in the same general direction. Grains are oriented alike when similar axes are parallel, and are oriented differently when similar axes make an angle with one another. The examination of a polished and etched surface of a pure metal shows that these crystals vary in color. Furthermore, if we rotate the specimen we find that these colors vary in intensity; some flash up while others die down. This phenomenon is known as the "oriented luster" of the metal or the "rotation effect." To illustrate, let Fig. 200 represent a microscope *B* and a prepared surface *A* illuminated by oblique light. Rays 1 and 2, falling on the flat surface, are reflected outside the field of the eyepiece and appear dark to the observer. Rays 3 and 4, striking the inclined surface, are almost totally reflected into the eyepiece and appear bright to the observer. Other grains may vary between these two extremes, according to the position of the axes.

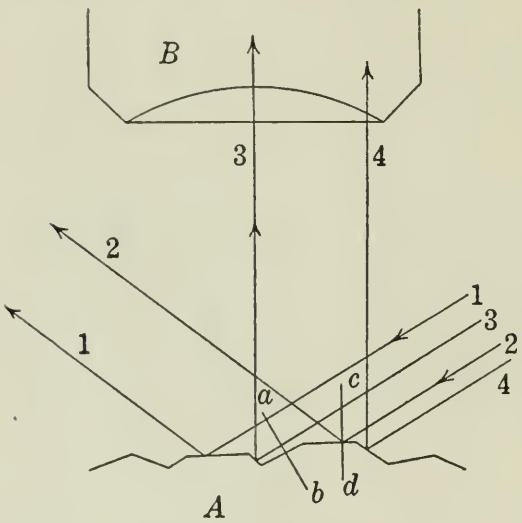

FIG. 200. Orientation

Why should these faces make various angles with each other? Why are they not all in the plane of polishing? The reason for this is not altogether clear, but we believe that when the specimen is polished the grains or crystals are worn down at different rates. We know that crystals have "directional" properties; that is, the hardness along one crystal axis may be different from the hardness along another. One crystal, for example, may have its axis tilted like *ab*, while another may be tilted like *cd*. Polishing tends to fill up the inequalities in the surface with débris from the metal and from the polishing medium. Etching, on the other hand, clears this away, leaving the crystal faces tipped as shown. It is clear, then, that as this specimen is rotated those faces whose crystal axis is not parallel to the axis of the microscope will show this "oriented luster."

Another property of a crystal is the presence of *cleavage planes*. If a pure metal is subjected to a stress which deforms it slightly, and then examined under the microscope, each crystal will be traversed by fine lines called slip bands. These lines are usually straight and parallel in the same grain, but have different directions in different grains. They will normally stop at the grain boundaries. These lines are not actual cracks in the metal, but simply steps formed by the slight deformation. Some authorities believe that such deformation causes the formation of amorphous metal similar to that supposed to exist between grains. Differently oriented and small grains promote strength, for failure along the cleavage plane in one crystal will stop when it encounters the difficultly cleavable face of the next and differently oriented grain.

698. Amorphous solids. In an amorphous solid the atoms are arranged with no regard to order, — the exact opposite of the crystalline state. A few solids, such as pitch and glass, and all molten metals, gases, and liquids are amorphous. Some consider such amorphous solids as undercooled liquids of high viscosity. It is believed that the metal which solidifies last from the molten state (represented by the dark lines in Fig. 215) is amorphous because when it crystallized there was no longer room for an orderly arrangement of the atoms in the characteristic space lattice. When a substance can exist in both states, the tendency is toward the crystalline one. Silica combustion tubes, for example, on prolonged heating become weak and fragile, owing to crystallization.

699. Preparation of metallographic specimens. The metal, if not too hard, is first sawed across at the point selected for examination. This face is then made flat with a file or with an emery wheel. If too hard for sawing, the metal is broken with a sledge hammer and a flat surface worked down with carborundum. It is essential for the success of the subsequent operations that the first rough surface be a plane. Grinding is then continued by rubbing the surface on different grades of emery cloth supported on a perfectly flat surface. Usually the specimen is turned through 90 degrees between grades of cloth so that the operator may be sure that he has removed all the scratches from the previous grade before he starts on the succeeding one. Polishing, the next step, is performed on a rapidly rotating horizontal

wheel covered with broadcloth. This cloth is impregnated with a suspension, in water, of fine rouge or levigated alumina. This polishing is continued until an examination under the microscope shows that the surface is free from scratches. It is then ready for etching, — the next step. Etching may be defined as a selective chemical action by which one of the constituents of the specimen is affected more than or in a different way from the others. The chemicals commonly used are as follows:

For iron and steel: an alcoholic solution of nitric acid (nitol), picric acid, hydrochloric acid, and cupric ammonium chloride.

For copper alloys: ferric chloride, nitric acid, ammonia, and bromine.

For lead alloys: hydrochloric acid, sodium hydroxide, and hydrofluoric acid.

For aluminum alloys: hydrochloric acid, sodium hydroxide, and hydrofluoric acid.

Sometimes a differential coloring may be obtained simply through the application of heat (heat tinting).

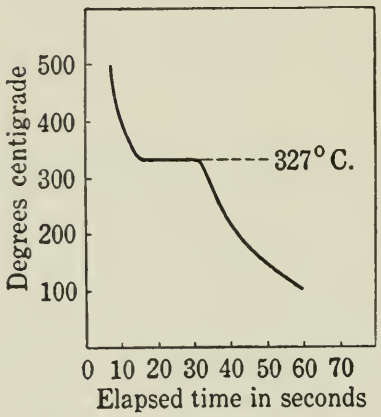

FIG. 201. Cooling curve of pure lead

700. Cooling curves. When a pure metal is raised to a temperature above its melting point and then allowed to cool slowly, certain characteristic changes take place. If we observe the temperature during equal intervals of time, and plot these as ordinates and the time intervals as abscissas, we obtain a curve such as is shown in Fig. 201. This curve (for lead) shows that the melt cools at a nearly constant rate until it reaches a temperature of 327° C., the melting point of pure lead. At this point, owing to the release of the latent heat of fusion, the curve remains horizontal for an appreciable length of time (until all the lead has solidified), after which the temperature again falls at a nearly constant rate. Bear in mind that this curve is for the pure metal; the presence of even small amounts of impurities will alter this curve by introducing other points of recalescence. For the purpose of this text such modifications of the simple cooling curve may best be studied under the following types:

1. Two metals which are insoluble in the solid state and insoluble in the liquid state.

2. Two metals which are insoluble in the solid state and soluble in the liquid state.

3. Two metals which are partially soluble in the solid state and soluble in the liquid state.

4. Two metals which are soluble in the solid state and soluble in the liquid state.

5. Two metals which form an intermetallic compound.

701. Type 1. This type of alloy, sometimes called the two-layer alloy, while not important industrially, is the simplest possible condition and an easy one for the student to follow. Let us consider the cooling curves of pure lead, pure aluminum, and four alloys. Such curves, plotted with similar coördinates to the last curve, are shown in Fig. 202. Curve 1 indicates that when pure Al is cooled from above its melting point, it remains at a temperature of 658.7° C. for an interval of time depending upon the mass of the metal. The curve for lead, 6, has already been discussed. Alloys 2, 3, 4, and 5 give corresponding retardations in the cooling. Curve 4, for example, shows that the alloy cools from above its melting point at a nearly constant rate until a temperature of 658.7° C. is reached, when it remains constant while the Al is solidifying. When all the Al has solidified, the mass cools at a constant rate until a temperature of 327° C. is reached, where another retardation takes place. When all the lead has solidified, the mass cools at a constant rate to room temperature. Owing to the difference in specific gravity and to the fact that the two metals are insoluble, this alloy on solidifying will consist of two layers, — the Al above, the Pb below.

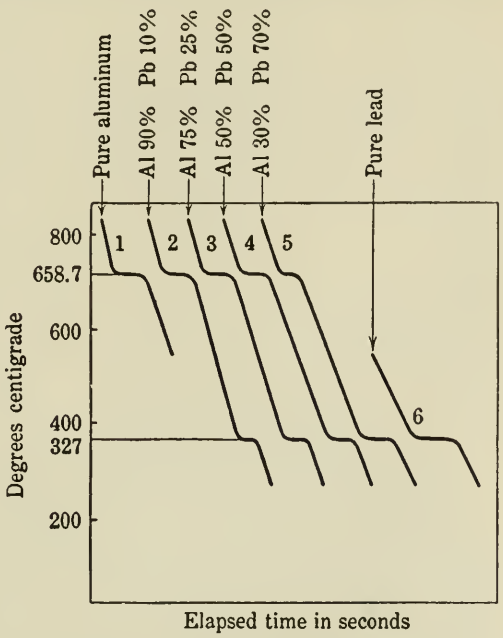

FIG. 202. Cooling curves of Al, Pb, and four alloys

A simple cooling curve of this type gives us no information regarding other alloys of these two metals. Let us now plot

this same data with a different system of coördinates, — this time with temperatures as ordinates and percentage composition as abscissas. Such a curve is known as an equilibrium diagram and is shown in Fig. 203. Let us consider alloy x, for example, containing 45 per cent of Al and 55 per cent of Pb, as it cools from above 700° C. This diagram tells us that above 658.7° C. all is liquid. On reaching this temperature crystals of Al come out of the melt and remain suspended in the molten lead. The temperature falls until 327° C. is reached, when crystals of Pb come out of the melt, and if this melt is stirred vigorously during solidification, it will finally consist of an intimate mixture of these two crystals.

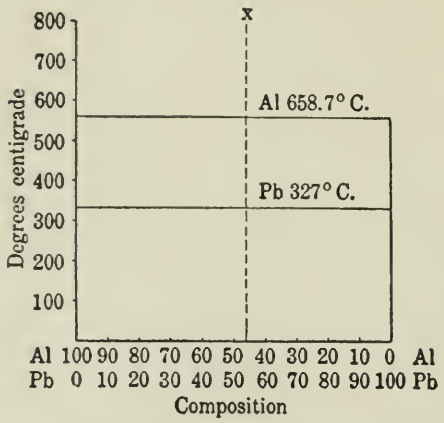

FIG. 203. Pb-Al equilibrium diagram

702. Type 2. It is a well-known fact that small quantities of impurities lower the melting point of most metals. For example, pure iron melts at a temperature of 1530° C., but the addition of small amounts of C, Si, Mn, etc. progressively lowers the melting point. Some ferrous alloys melt at as low a temperature as 1130° C. Let us now consider the equilibrium diagram of the Pb-Sb system shown in Fig. 204.*

This diagram indicates that Sb melts at a temperature of 630.5° C. and Pb at a temperature of 327° C. The addition of small amounts of Sb to Pb progressively lowers the melting point of the alloy to a minimum of 248° C. The addition of small amounts of Pb to Sb progressively lowers the melting point of the alloy to the same minimum. We call this alloy of lowest melting point the eutectic or eutectic alloy, and in this case it contains 87.5 per cent of Pb and 12.5 per cent of Sb. The point E is called the eutectic point, and the line CED the eutectic line. The line AEB is called the liquidus and the line CED the solidus, since all alloys above the former are liquid and those below the latter solid.

Let us now consider three alloys, 1, 2, and 3, containing, respectively, 93, 87.5, and 40 per cent of Pb. Alloy 1 cools from

*Recent work of R. S. Dean has altered this equilibrium diagram slightly.

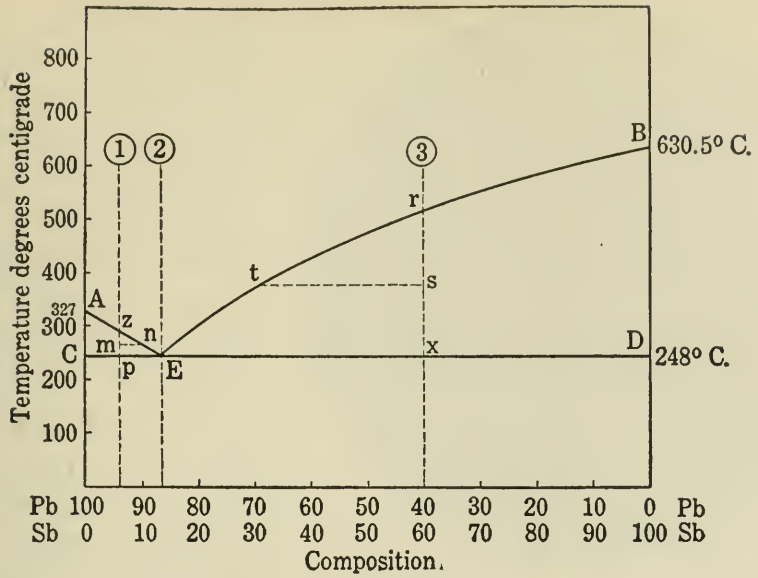

FIG. 204. Pb-Sb equilibrium diagram

above the melting point of the alloy until its composition ordinate intersects the curve *AE*. At this point, *z*, pure lead begins to come out of solution. As the temperature falls, more lead comes out of solution, and the liquid thus impoverished in Pb changes along the line *AE*. This continues with falling temperature until the remaining liquid reaches a composition of 87.5 per cent Pb, when it solidifies as the eutectic, — an intimate mixture of Pb and Sb. In the brief interval while this eutectic is solidifying the temperature of the whole mass remains constant, as in the case of a pure metal. At temperature *m* the mass will consist of crystals of Pb suspended in a liquid of composition *n*. At a temperature of 200° C. the mass will consist of crystals of Pb in a ground

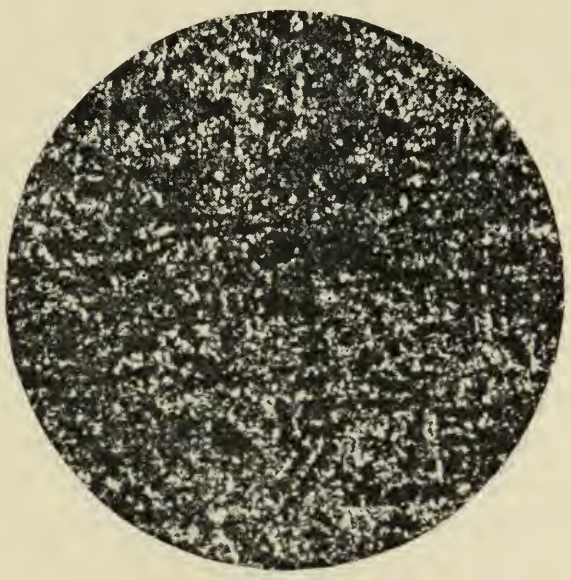

FIG. 205. Sb—10 per cent; Pb—90 per cent. (× 100)

Photograph by Dr. V. O. Homerberg

FIG. 206. Sb — 12.5 per cent; Pb — 87.5 per cent. (× 100)

Photograph by Dr. V. O. Homerberg

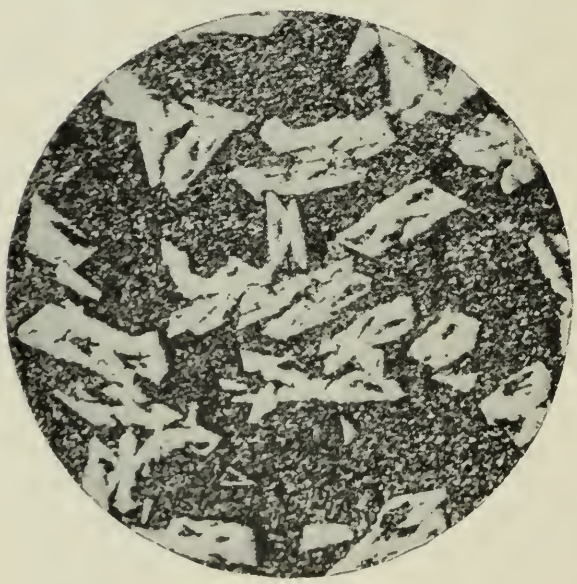

FIG. 207. Sb — 30 per cent; Pb — 70 per cent. (× 100)

Photograph by Dr. V. O. Homerberg

mass of the eutectic, — a structure shown in Fig. 205. Alloy 2 cools from the liquid state until it reaches point *E*, when it solidifies as the eutectic alloy (an intimate mixture of Pb and Sb) with excess of neither Pb nor Sb, — a structure shown in Fig. 206. Alloy 3 cools from the liquid state until it reaches a temperature represented by the point *r*, when minute crystals of pure antimony begin to come out of solution. As the alloy cools further, Sb continues to come out of solution, and the liquid thus impoverished in Sb changes along the curve *BE*. At a temperature represented by the point *s* the alloy will consist of a mushy mass of crystals of Sb suspended in a liquid whose composition is represented by the point *t*. Finally, when the composition of the remaining liquid reaches 87.5 per cent Pb, it solidifies as the eutectic. At a temperature of 200° C. a polished and etched section will appear as in Fig. 207, — that is, crystals of excess antimony in a ground mass of the eutectic.

703. Solid solution. We have been dealing, up to this point, with metals soluble in the liquid state but insoluble in the solid state. We come now to a new conception, — two metals partially soluble in the solid state. It is often difficult for the beginner to visualize this condition, — a solid solution. Let us take a solid solution of silver and gold and compare it to the more common aqueous solution of alcohol. If we take one pound of silver at 960° C. and one pound of gold at 1080° C., and mix them together, we shall have a perfectly homogeneous, fluid mass. The atoms of the silver are uniformly dispersed through the liquid gold, just as the atoms of alcohol are uniformly dispersed through the water. If we allow this molten alloy to cool, when it reaches 1050° C. it solidifies, but there is no separation of the two constituents, as in the alloy types heretofore studied. Even in the solid state the atoms of silver are uniformly dispersed through the gold, and microscopic examination shows that this alloy consists of polygonal grains of solid solution similar to the polygonal grains of pure metal. As a matter of fact, it is often impossible to distinguish one from the other. The following alloys are among those forming such solid solutions: gold-platinum, nickel-chromium, iron-cobalt, iron-manganese, iron-nickel, tungsten-molybdenum. While the solid solution thus formed is usually crystalline, it may be amorphous, like glass, which is a solid solution of SiO_2, CaO, Na_2O, PbO, etc. The lack of orderly arrangement of the atoms in such amorphous solids has already been pointed out.

704. Type 3. This class of alloys is made up of those metals which are completely soluble in the liquid state and partially soluble in the solid state. Let us consider as an example the equilibrium diagram of the Ag-Cu system shown in Fig. 208. This indicates that Ag and Cu are soluble in all proportions in the liquid state. In the solid state Ag will hold in solution 6 per cent of Cu, and Cu will hold in solution 2 per cent of Ag. A eutectic is formed consisting of an intimate mixture of these two solid solutions. This eutectic contains 71.9 per cent of Ag and melts at 778° C. We will call the silver-rich alloy α and the copper-rich alloy β. *AEB* is the liquidus and *ACEDB* the solidus.

Alloy 1 (containing 96 per cent of Ag) cools from the liquid state until it reaches a temperature represented by point *p* on

the liquidus. At this temperature crystals of a solid solution of composition q will come out of solution. This reduces the percentage of Ag in the liquid, and with falling temperature the composition of the liquid will follow AE, and that of the solid solution, AC. Finally, at temperature r, the whole mass will be solid as a solid solution containing 96 per cent of Ag. Actually, the last bit of solution to solidify must have a composition t, but at this temperature, so near the melting point of the alloy, there is complete diffusion of this through the already solidified mass. There will be no eutectic formed.

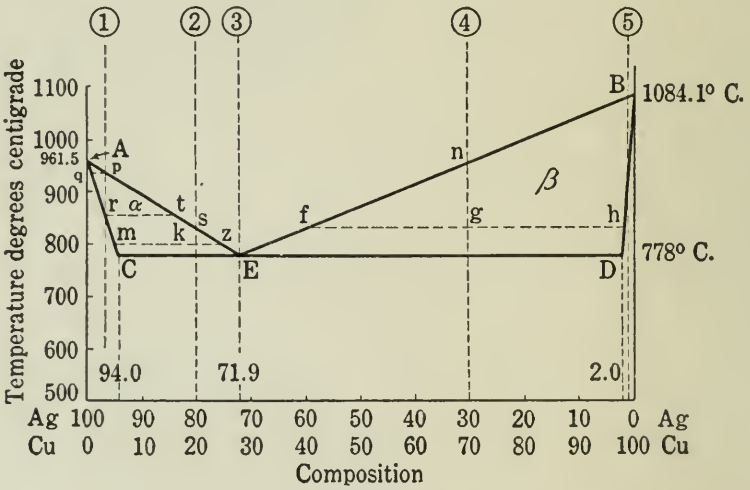

FIG. 208. Ag-Cu equilibrium diagram

Alloy 2 (containing 80 per cent of Ag) cools from the liquid state until it reaches temperature s, when solid solution begins to come out of the liquid. With falling temperature this solid solution will continue to come out. At temperature k the mass will consist of crystals of solid solution of composition m suspended in a liquid of composition z. As the temperature falls the composition of the liquid will follow AE, and that of the solid solution, AC, until, at the eutectic temperature, the remaining liquid will solidify as eutectic. At room temperature the alloy will consist of solid solution α suspended in a ground mass of the eutectic. This eutectic is an intimate mixture of solid solutions α and β.

Alloy 3 cools from the liquid state, without change, until it reaches 778° C., when the whole mass solidifies as the eutectic, — an intimate mixture of solid solution α and solid solution β.

Alloy 4 (containing 30 per cent of Ag) cools from the liquid state until it reaches temperature n, at which point solid solution β begins to crystallize from the liquid. This solid solution continues to come out, until at temperature g the mass will consist of crystals of a solid solution of composition h suspended in a liquid of composition f. On further cooling, the composition of the solid solution will follow BD, and that of the liquid, BE, until at 778° C. the latter will solidify as eutectic. At room temperature the alloy will consist of excess β in a matrix of eutectic.

Alloy 5 (containing 99 per cent of Cu) cools from the liquid state until its composition ordinate cuts the liquidus, when solid solution begins to come out of liquid solution. Freezing continues in a manner similar to Alloy 1 until at room temperature it will consist of a solid solution containing 99 per cent of Cu.

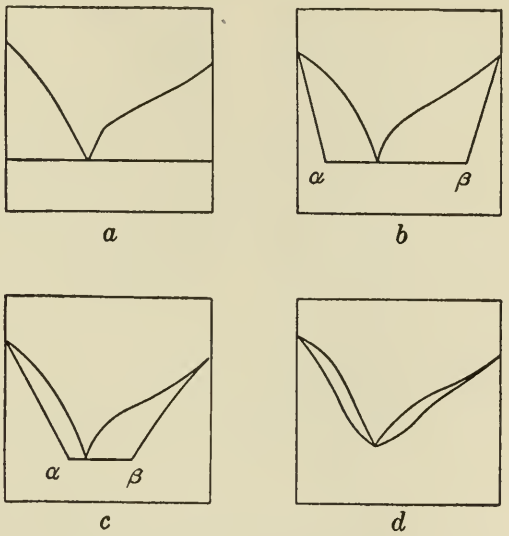

FIG. 209. Development of solid solution

705. Type 4. The diagrams in Fig. 209 indicate the development of an alloy of two metals which are completely soluble in the liquid state and completely soluble in the solid state; that is, which consist entirely of a solid solution. a represents a Type-2 alloy in which a eutectic of the two pure metals is formed; b, the Type-3 alloy in which the metals are partially soluble and the eutectic is one composed of the two solid solutions; c, an alloy in which the two metals are slightly more soluble; d, an alloy in which the two metals are completely soluble in the solid state and no eutectic is formed, but simply an infinite series of solid solutions.

As an example of Type 4 we will take the Cu-Mn system shown in Fig. 210. Alloy 1 contains 80 per cent of Cu. It cools from the liquid state until it reaches point f, when a solid solution of composition g begins to come out of solution. On further cooling, solid solution continues to come out of the liquid, the composition of the solid solution changing along $AghE$, and the

composition of the liquid along *AfkE*, until at temperature *h* the whole mass will become solid as a solid solution containing 80 per cent of Cu. Actually the last bit of liquid to solidify will have a composition *k*, but under ordinary conditions of cooling complete diffusion will take place.

Alloy 2 contains 30 per cent of Cu. It cools from the liquid state until it reaches *z*, when a solid solution of composition *m* begins to come out of liquid solution. At temperature *n* the mass will consist of crystals of solid solution of a composition *o*

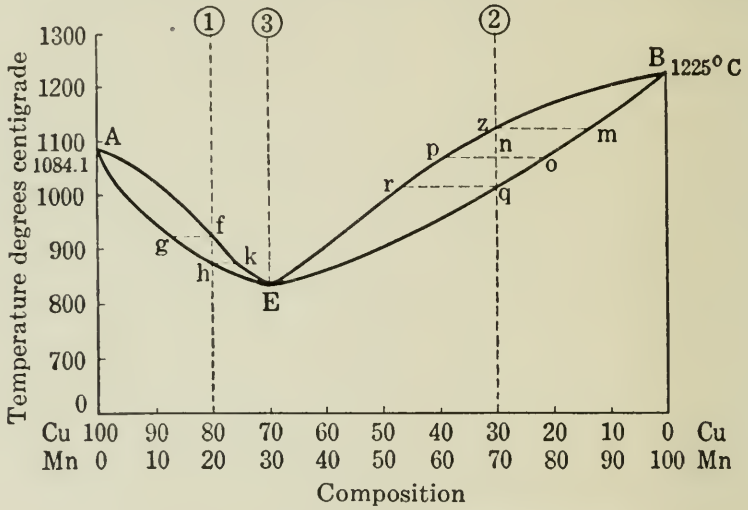

FIG. 210. Cu-Mn equilibrium diagram

suspended in a liquid of composition *p*. Finally, at temperature *q*, the whole mass will become solid as a solid solution containing 30 per cent of Cu.

Alloy 3 cools from the liquid state with no change until temperature *E* is reached, when the whole mass solidifies as a solid solution, this time the solid solution with the lowest melting point of the whole series, *but not a eutectic*.

706. Type 5. We now come to a type of diagram that is often hard for the student to understand,—that is, one in which an intermetallic compound is formed. A great many metals are capable of forming compounds such as $SbCu_3$, $SbCu_2$, $NaZn_{11}$, which do not conform to the laws of valence. Their exact nature is as yet imperfectly understood.

Let us take as an example of this type of alloy the Mg-Sn series, the equilibrium diagram of which is shown in Fig. 211. This diagram tells us that Sn and Mg form a definite compound

of a composition $SnMg_2$, and that it also forms two eutectics: one which we shall call *K*, composed of pure Mg and the intermetallic compound $SnMg_2$; the other which we shall call *L*, composed of pure Sn and the intermetallic compound $SnMg_2$.

Alloy 1, containing 80 per cent of Mg, cools from the liquid state until it reaches temperature *o*, when pure Mg begins to come out of solution. On further cooling, Mg continues to come out of solution, and the liquid thus impoverished in Mg changes in composition along the line *AE*. Finally, when temperature *r*

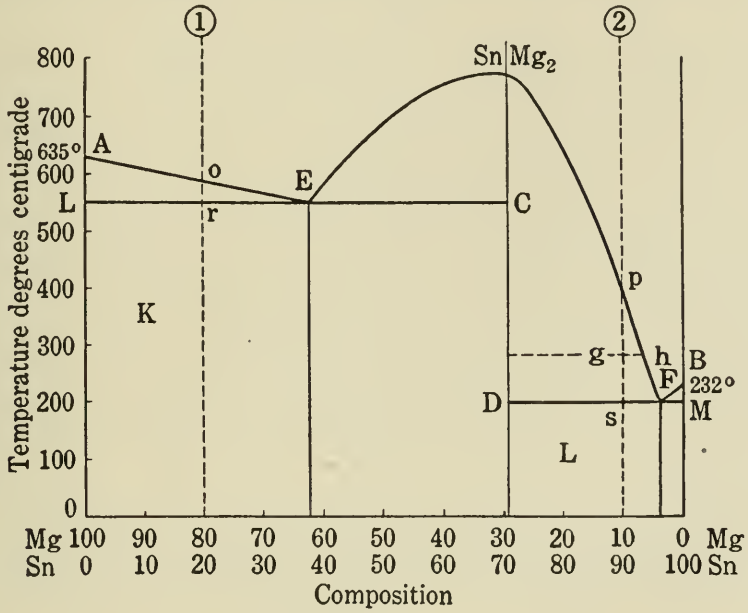

FIG. 211. Mg-Sn equilibrium diagram

is reached, the remaining liquid will solidify as eutectic *K*. At room temperature the mass will consist of excess Mg suspended in a matrix of eutectic *K*.

Alloy 2, containing 10 per cent of Mg, cools from the liquid state until temperature *p* is reached, when crystals of the intermetallic compound $SnMg_2$ begin to come out of solution. With falling temperature this continues to take place until at temperature *g* the mass will consist of crystals of $SnMg_2$ suspended in a liquid of composition *h*. Finally, at temperature *s*, the remaining liquid will solidify as eutectic *L*, and at room temperature the alloy will consist of excess $SnMg_2$ in a matrix of eutectic *L*.

707. Eutectoid. It now remains to show how a eutectic-like mass may form in an alloy while it is in the solid state. Such a

mass is termed a eutectoid, since it has some of the properties of the eutectic. Fig. 212 is the equilibrium diagram of two metals, A and B, which are completely soluble in the liquid state and completely soluble in the solid state; that is, they form an unbroken series of solid solutions. These solid solutions, however, break up as indicated in the lower part of the diagram. For example, let us take any alloy such as (1) (containing 80 per cent of A) and cool it from the liquid state. At point *l* a solid solution

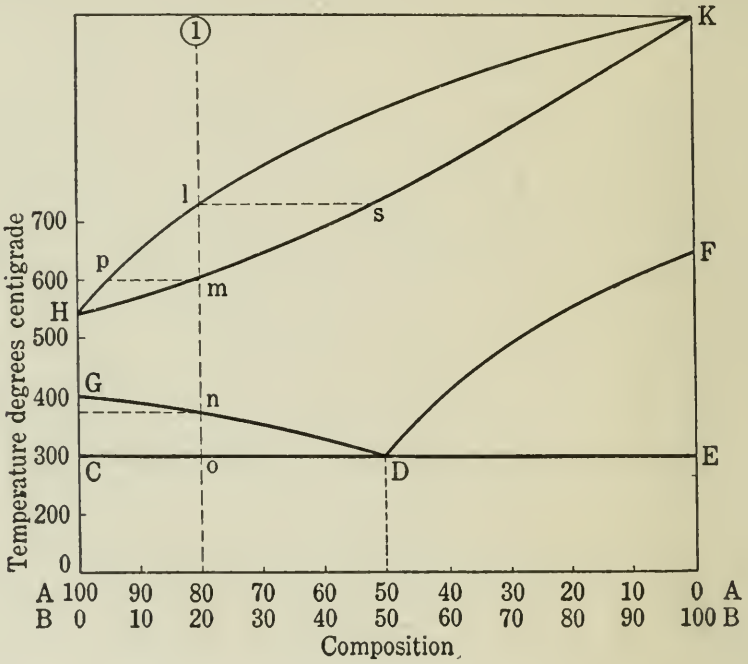

FIG. 212. Formation of a eutectoid

of composition *s* comes out of the liquid solution, and as the temperature falls the composition of the solid solution follows curve *KsmH*, while that of the liquid follows *KlH*, until at temperature *m* the whole mass solidifies as a solid solution of composition (1). As the temperature continues to fall no change takes place until *n* is reached, at which point crystals of the pure metal A begin to come out of the solid solution. As the metal cools, crystals of A continue to come out. The solid solution thus impoverished in A follows the curve *GnD*. At temperature *o* the solid solution will break up into a eutectoid which consists of a very intimate mixture of the pure metals A and B. At room temperatures Alloy 1 will consist of crystals of the pure metal A suspended in a ground mass of the eutectoid.

IRON-CARBON ALLOYS

708. General. We come now to a consideration of steels and cast irons which are binary alloys of iron and carbon. Actually these alloys always contain small amounts of Mn, Si, P, and S, and often V, Cr, W, and Ni as well. It is impossible, however, with the methods now at our disposal, to show the structural changes in such complex alloys by simple line diagrams. In order to simplify the text for the student we will consider these

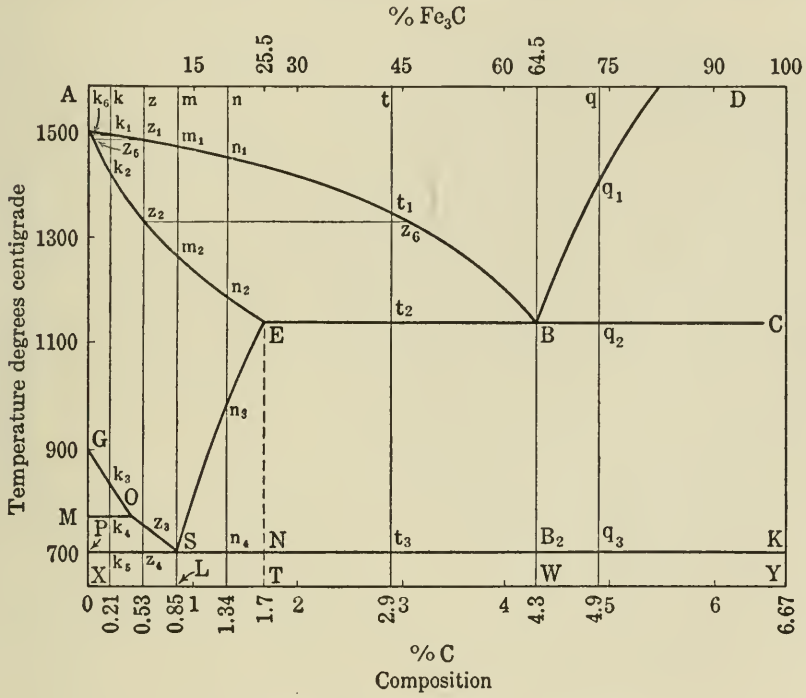

FIG. 213. Fe-C equilibrium diagram

steels and cast irons as simple alloys of iron and carbon. Iron and carbon at high temperatures (above 1300° C.) react to form iron carbide (Fe_3C). This iron carbide is completely soluble in liquid iron and partially soluble in solid iron. Iron carbide contains 6.67 per cent of carbon, so that an alloy of this carbon content would theoretically consist entirely of Fe_3C. Actually, however, this never occurs, owing to the decomposition of the carbide.

709. Iron-carbon equilibrium diagram. Fig. 213 shows the complete iron-carbon equilibrium diagram. Curve *AEBC* is the solidus, and curve *ABD* the liquidus. Curve *GOS* is called the

ferrite solubility curve, and line *SE* the cementite solubility line. *EBC* is the eutectic line, and *PSK* the eutectoid line. Before describing the changes occurring in the solid state on cooling, it is necessary to define the metallographic constituents of these alloys. They are dealt with so frequently in discussing steels that instead of calling them solid solution A or eutectoid, for example, we call them austenite and pearlite.

710. Allotropic forms of pure iron. If a piece of pure electrolytic iron is heated to a temperature of 1100° C. and then allowed to cool slowly, we find that the cooling curve of this metal is not an unbroken line such as other metals exhibit in cooling from below their melting point. This piece of iron will cool at a constant rate until a temperature of about 900° C. is reached, when there will be a break in the curve, the temperature of the piece remaining constant for a brief interval although the furnace itself is cooling. Heat must therefore be evolved within the piece. On further cooling, another, and this time a slight, retardation will take place at 768° C., after which the piece will cool at a uniform rate until room temperature is reached. The cooling curve is shown in Fig. 214. These evolutions of heat indicate certain changes in the nature of the iron, — as we now believe, the passage from one allotropic form of iron to another. At the present time all scientists recognize the existence of alpha and gamma iron; many others believe that a third, beta iron, exists; and a still smaller school claim to have proof of the existence of a fourth allotrope, — delta iron.

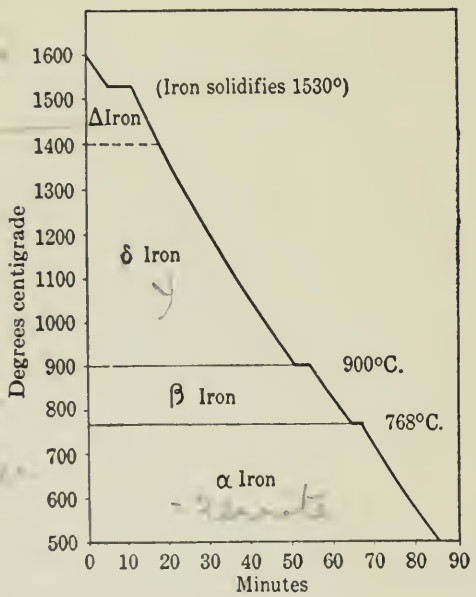

FIG. 214. Cooling curve of pure iron

There are also marked changes in some of the physical properties of iron in passing from one allotropic form to another. Delta iron is stable above 1400° C. Its existence is doubtful, and its properties, aside from the fact that it is body-centered, have not been determined. The modification gamma iron is

face-centered, beta iron is body-centered, and alpha iron is also body-centered. The internal energy, electrical conductivity, magnetism, heat conductivity, and volume of these modifications differ. For example, a little below 768° C. iron is strongly magnetic; at higher temperatures it is practically nonmagnetic.

711. Ferrite. This is the name given by metallurgists to carbon-free iron in the alpha state. It has a tensile strength of about 40,000 pounds per square inch and a Brinell hardness of about 80. Ingot iron and wrought iron are mostly ferrite. Fig. 215* shows the polygonal grains of this constituent.

FIG. 215. Electrolytic iron. (× 100)

Photograph by Dr. V. O. Homerberg

712. Cementite. This is the name given to the carbide of iron (Fe_3C). It is very hard and brittle. To its presence is probably due, in a large measure, the hardening power of steel.

713. Austenite. This is the name given to those solid solutions in which gamma iron is the solvent. When the iron is molten, the carbon is completely soluble in the iron. This solubility, like that of salt in water, decreases with falling temperature until, at 1130° C., the iron will hold in solution only 4.3 per cent of carbon. In the solid state iron will hold in solution 1.70 per cent of carbon at 1130° C. and practically none at atmospheric temperature. We see, then, that the constituent austenite may contain any amount of carbon up to 1.70 per cent. When it contains 1.70 per cent of carbon, it is termed saturated austenite.

714. Pearlite. This is a eutectoid consisting of alternate plates of cementite and ferrite and containing about 0.85 per cent of carbon. It derives its name from the pearlitic luster

* Unless otherwise stated, the etching reagent used in the preparation of all specimens was nitol.

which the structure imparts to the polished surface. Under the microscope it appears as shown in Figs. 216 and 219. In etching, the acid attacks the soft ferrite but does not attack the cementite, so that it stands out in relief and appears white to the eye. A steel containing 0.85 per cent of carbon is termed a eutectoid steel; one containing less than this amount, hypo-eutectoid steel; and one containing more than this amount, hypereutectoid steel.

FIG. 216. Pearlite. (× 500)

Photograph by Bausch and Lomb Optical Company

715. The transformation points. The temperatures at which the various allotropic changes occur are called the transformation points or critical points. The method of naming these is borrowed from the French. For example, the *arrêt refroidissement*, or retardation on cooling, is designated as the *Ar* point, followed by subscript numeral to indicate which point we are talking about. The halt on heating is termed the *Ac* point, from *arrêt chauffage*. In general the *Ac* points are from 20 to 40° C. higher than the *Ar* points (depending upon the rate of cooling or heating and the chemical composition of the metal). The critical points, indicated in Fig. 213, may be summarized as follows:

	ON COOLING	ON HEATING
GO	Ar_3	Ac_3
OS	Ar_{3-2}	Ac_{3-2}
MO	Ar_2	Ac_2
PS	Ar_1	Ac_1
SE	Ar_{cm}	Ac_{cm}
SK	Ar_{3-2-1}	Ac_{3-2-1}

By critical range is meant the range of temperature covered by the critical points A_3, A_2, and A_1, — that is, *GOSK* in Fig. 213.

CHANGES IN STEEL ON COOLING

716. General. Let us now follow the changes which take place on slowly cooling four representative steels from the liquid condition to room temperature. Bear in mind that these are *slowly* cooled; quenching or more rapid cooling will bring about an entirely different set of structures. Let these steels contain 0.21, 0.53, 0.85, and 1.34 per cent of carbon respectively, and be represented in Fig. 213 by the ordinates k, z, m, and n.

717. Low-carbon steel. The 0.21 per cent of carbon steel will remain molten (a solution of carbon in molten iron) until point k_1 (1495° C.) is reached, when austenite begins to come out of solution. This austenite will have a composition corresponding to point k_6 on curve AE. The separation of this austenite leaves the molten metal richer in carbon. As the temperature falls, austenite of increasing carbon content comes out of the solution, until at k_2 (1395° C.) the whole mass is solid as austenite containing 0.21 per cent of carbon. On further cooling no change, except diffusion of the carbon, takes place until k_3 (850° C.) is reached, when gamma iron changes to beta iron and this comes out of solution. At k_4 the beta changes to alpha, and this continues to come out of solution as ferrite. The austenite, thus enriched in carbon, follows the curve GOS until at 0.85 per cent carbon it changes into the eutectoid pearlite. No further changes take place in cooling to room temperature. This structure will then consist of grains of ferrite surrounded with a network of pearlite, as shown in Fig. 217.

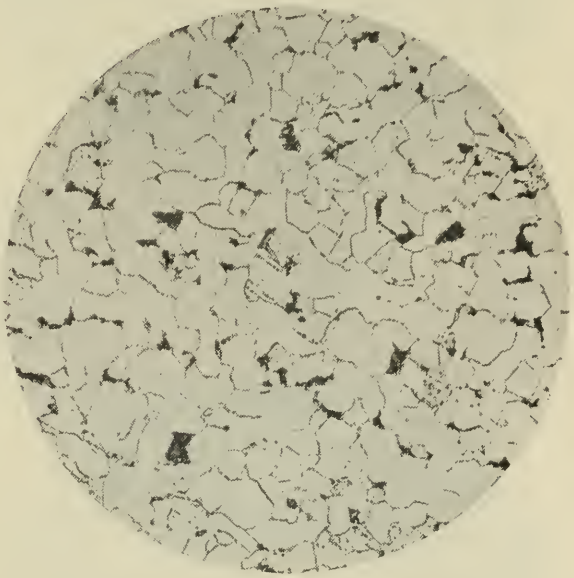

FIG. 217. Low-carbon steel (ferrite and pearlite). (× 100)

Nitol etch

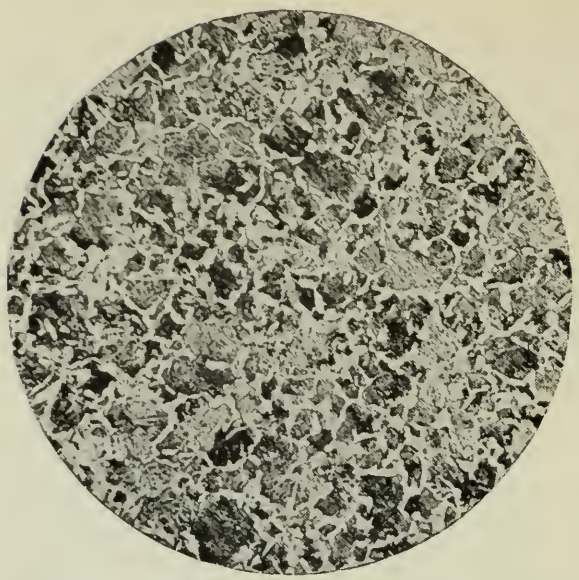

FIG. 218. Medium-carbon steel (ferrite and pearlite). (× 100)

Nitol etch

FIG. 219. Pearlite. (× 500)

Nitol etch. (Photograph by Dr. V. O. Homerberg)

718. Medium-carbon steel. The 0.53 per cent carbon steel remains molten until z_1 (1480° C.) is reached, when austenite of composition z_5 comes out of solution. Between z_1 and z_2 it will consist of a mushy mass of austenite crystals suspended in the molten alloy. During this interval the liquid will change along curve AB, the austenite along AE. The last metal to solidify at z_2 will have a composition z_6, but as the temperature falls between z_2 and z_3 there will be complete diffusion, leaving unsaturated austenite containing 0.53 per cent of carbon. At z_3 the gamma iron begins to change to alpha, and ferrite comes out of solution. This continues until the austenite has a composition of 0.85 per cent carbon, when it changes abruptly into pearlite. At z_4, then, the mass will consist of crystals of ferrite surrounded by the eutectoid pearlite. Cooling to room temperature produces no further change. This structure is shown in Fig. 218.

719. Eutectoid steel. The 0.85 steel will cool to m_1 (1480° C.), when austenite begins to separate out. This separation con-

tinues, with falling temperature, the composition of the melt changing along AB and that of the solid austenite along AE until the whole mass is solid at m_2 (1250° C.). When the temperature reaches S (700° C.) the austenitic mass changes into the eutectoid pearlite. The steel at room temperature will consist entirely of this structure, as shown in Fig. 219.

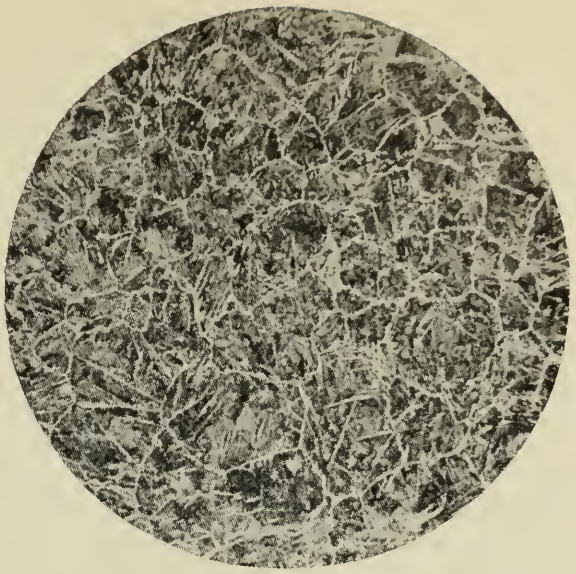

FIG. 220. High-carbon steel (cementite and pearlite). (× 100)

Nitol etch. (Photograph by Dr. V. O. Homerberg)

720. High-carbon steel. The 1.34 per cent carbon steel will cool until n_1 is reached, when austenite begins to come out of solution. In cooling below n_1 austenite (of increasing carbon content) continues to separate out until the whole mass is solid at n_2 (1190° C.). Diffusion of the carbon progresses as the austenite cools along n_2–n_3. At n_3 (930° C.) excess cementite begins to separate out of solution. The austenite, being thus impoverished in carbon, follows curve SE until it has a composition of 0.85 per cent carbon (at n_4), when it changes into pearlite. The mass at room temperature will consist of excess cementite and pearlite, as shown in Figs. 220 and 221. Note that the sodium picrate etches the cementite.

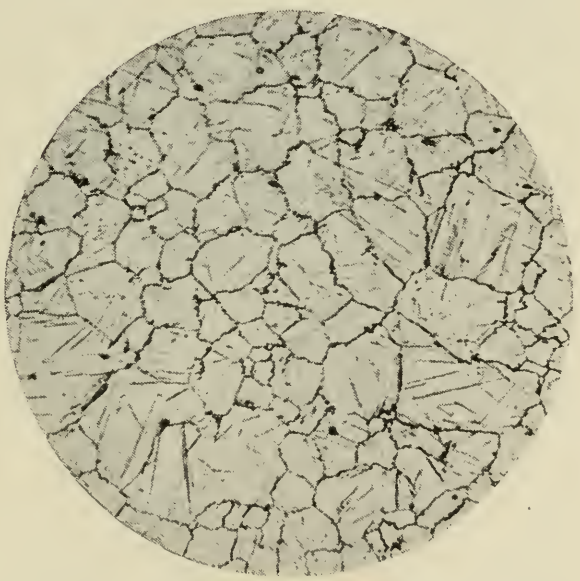

FIG. 221. High-carbon steel (cementite and pearlite). (× 100)

Sodium-picrate etch

CHANGES IN CAST IRON ON COOLING

The dividing line between steel and cast iron has been taken as 1.70 per cent carbon merely as a matter of convenience. Actually most steels contain less than this amount, while a very few special ones may contain slightly more. Let us now consider the changes taking place on cooling representative cast irons. Referring to Fig. 213, bear in mind that *ABD* is the liquidus and *AEBC* the solidus. All alloys between these two lines are part solid, part liquid (mushy stage). The line *EBC* is the line of the eutectic (austenite and cementite). The line *PSK* is the line of the eutectoid (cementite and ferrite), that is, pearlite. The eutectic point *B* is 4.3 per cent carbon, the alloy of lowest melting point, 1130° C. Like the steels, cast irons are divided into hypo-eutectic and hypereutectic, according to the carbon content. The former contain less than 4.3 per cent of carbon; the latter, more than that amount.

721. Stable versus metastable condition. The diagram shown in Fig. 213 is known as the metastable equilibrium diagram. This assumes that all the carbon in the steel is in the form of Fe_3C, but this is often not the case. In many cast irons, particularly those containing high percentages of carbon or certain impurities, there is a tendency for the cementite to break up into graphite and ferrite (the stable state). This can be shown on the diagram, but it would only serve to confuse the student attempting to understand the more simple condition.

722. Hypo-eutectic cast iron. Let us now follow the solidification of a cast iron containing 2.9 per cent of carbon. This will remain liquid in cooling from, let us say, 1600° C., until it reaches point t_1 (1280° C.), when crystals of austenite come out of solution. The austenite continues to come out until point t_2 (1130° C.) is reached, when the remaining liquid solidifies as a eutectic (austenite and cementite). In order to distinguish one from the other (they differ only in source) we give to the austenite which separates from the liquid the name *primary austenite*, and to that of the eutectic the name *eutectic austenite*. The same system of nomenclature is used for cementite. As the solid cools from t_2 to t_3, cementite separates out from the primary austenite and from the eutectic austenite, for curve *SE* tells us that at these temperatures austenite can-

not hold in solution 1.70 per cent of carbon. This cementite is termed *pro-eutectoid* in contrast to the cementite which may have already separated out in the formation of the eutectic. Finally, at 700° C., the austenite is of eutectoid composition and changes to pearlite. Below t_3 the metal will consist of eutectic cementite, pro-eutectoid cementite, and pearlite.

723. Eutectic cast iron. Let us now follow the changes in a eutectic iron (4.3 per cent carbon) on slow cooling. This alloy will remain liquid until it reaches B (1130° C.), at which temperature the whole mass will solidify as eutectic (austenite and cementite). On further cooling cementite will be rejected from the austenite along the curve SE until the remaining austenite at B_2 (700° C.) contains 0.85 per cent of carbon, when it changes into pearlite. Such an iron at room temperature will consist of eutectic cementite, pro-eutectoid cementite, and pearlite.

724. Hypereutectic cast iron. Let us now follow the changes, on slow cooling, in a cast iron containing 4.9 per cent of carbon as represented by q in Fig. 213. The molten metal will cool until it reaches q_1 (1430° C.), when cementite begins to come out of solution. Between q_1 and q_2 this excess cementite continues to come out of solution, and the melt thus impoverished in carbon follows curve BD. When the temperature has reached q_2 (1130° C.), the remaining liquid is of eutectic composition and the mass solidifies as this eutectic. On cooling from q_2 to q_3 (since austenite in this range cannot hold in solution 1.7 per cent of carbon) cementite separates out, the austenite following curve SE until it contains 0.85 per cent of carbon, when it changes to pearlite. Such an iron at room temperature will consist of primary cementite, eutectic cementite, pro-eutectoid cementite, and pearlite.

GRAPHITIZATION OF CAST IRONS

725. Decomposition of cementite. The cementite of cast iron is not a stable compound. It tends to break up into ferrite and graphite according to the following reaction:

$$Fe_3C = 3\ Fe + C.$$

The rate and extent of this dissociation will be determined by the following factors: (1) the rate of cooling from above the critical range; (2) the presence of much carbon; (3) the pres-

ence of silicon or impurities having similar action; (4) the presence of manganese and sulphur. Slow cooling, high carbon, high silicon, low manganese, and low sulphur promote the formation of graphite. The reverse conditions retard its formation. For example, it is difficult to obtain graphite in a steel, for it is usually not saturated with Fe_3C (contains less than 1.7 per cent of carbon), cools quickly, and has a low silicon content; but in a cast iron containing from 2.5 to 4.0 per cent of carbon and considerable silicon and cooling slowly in a sand mold, it is difficult to prevent the separation of graphite. This graphite lends a characteristic dark color to the otherwise white iron, so that cast irons are often classified, according to the color of a fresh fracture, as (1) white iron (nearly all combined carbon); (2) mottled iron (approximately 50 per cent combined carbon and 50 per cent graphite); (3) gray iron (nearly all graphite).

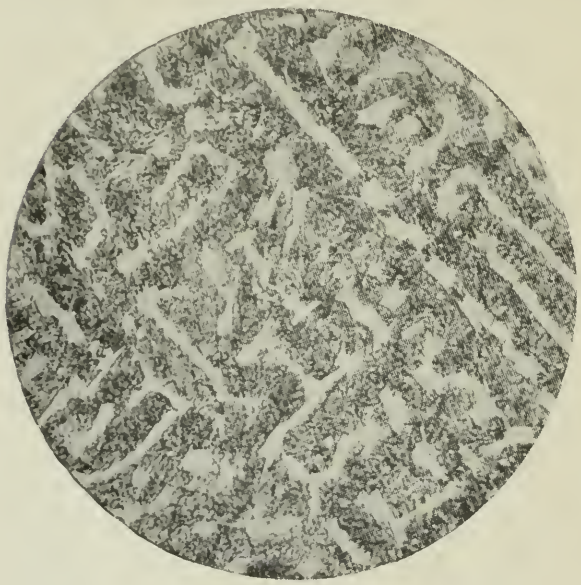

FIG. 222. White cast iron. (× 100)
Photograph by Dr. V. O. Homerberg

726. White cast iron. This is the white cast iron of commerce. As shown in Fig. 222, it consists of cementite and pearlite. Its structure and cycle of solidification are similar to the alloys just discussed under the iron-carbon equilibrium diagram. Owing to the presence of so much cementite these irons are very hard and brittle.

727. Gray cast iron. The other extreme is gray cast iron, in which most of the cementite has been dissociated into ferrite and graphite. Fig. 223 shows a photomicrograph of a specimen containing 2.5 per cent of carbon. The graphite occurs in flakes embedded in a hypo-eutectoid matrix. This sample contains considerable silicon, so that the normal breakdown of the cementite on slow cooling is accelerated. Consequently, on slow

cooling from the molten metal, all the eutectic cementite, nearly all the pro-eutectoid cementite, and part of the eutectoid cementite will be dissociated.

How does the presence of the graphite affect the physical properties of the alloy? A glance at the photomicrograph in Fig. 223 will show that a considerable percentage of the area is made up of graphite. This is accounted for by the fact that a cast iron containing 3 per cent by weight of carbon as graphite will contain over 12 per cent by volume of this constituent. Graphite itself is weak, and the presence of so many areas of graphite breaks up the continuity of the ferrite crystals. Gray cast irons are therefore brittle, weak, and not capable of being worked either hot or cold. The breaking-up of the ferrite crystals and the mere presence of the graphite promotes machinability. For maximum machinability and fair tensile strength the cast iron should have from 0.3 to 0.6 per cent of combined carbon, which is obtained with slow cooling and with from 1.5 to 3.0 per cent of silicon.

FIG. 223. Gray cast iron. (× 100)
Photograph by Dr. V. O. Homerberg

MECHANICAL TREATMENT OF STEEL

728. General. Every worker in the metal is familiar with the fact that rolling, hammering, and pressing have a profound effect upon the properties of steel. While such work is often intended only to shape the piece, at other times it is carried out with the object of enhancing some of the valuable properties of the metal.

729. Hot work versus cold work. For all steels (carbonless iron, of course, being excepted) the working of the metal by

mechanical means above its critical range is termed hot working; below its critical range, cold working. The effect of mechanical work can best be shown by Fig. 224. Bear in mind that above the critical range the metal is in the form of austenite, a solid solution, and is therefore capable of recrystallization, while below its critical range it has already assumed the crystalline form. In *A* we see that a crystal coming out of the molten

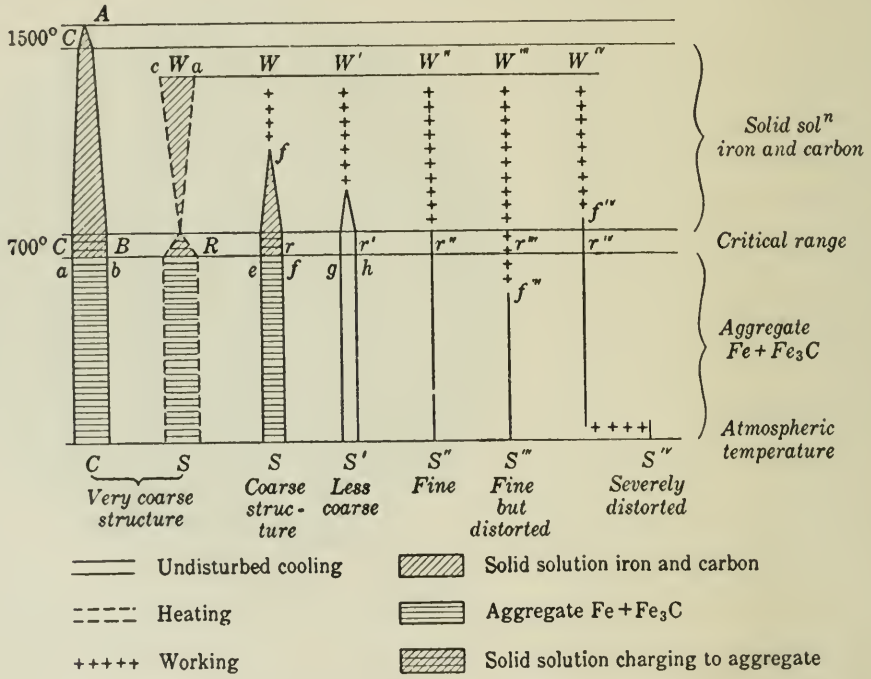

FIG. 224. Effect of mechanical treatment

After Sauveur

metal, as it cools slowly, will grow very rapidly during solidification, and less rapidly down to the critical range, where all growth ceases. The size of the crystal is comparable to the line *ab*. On reheating this alloy, as in *S*, the grain size remains the same until it reaches the critical range, where the aggregate (ferrite and pearlite in low-carbon steels, pearlite and cementite in high-carbon steels) is transformed into austenite. This immediately begins to crystallize, so that at *W* the grain size is comparable to *ac*. In the third case let us assume that as the piece cools from the solidification point mechanical treatment breaks up the crystals as they form, and grain growth does not have an opportunity to start until the mechanical work

ceases at *f*, with the result, as shown, of a much finer grain than in the first case. Finally, in *W''*, the maximum refinement of grain is obtained by working the piece just down to the critical range and then allowing it to cool undisturbed. Working below the critical range, as in *W'''*, simply distorts the pearlite matrix and serves no useful purpose. Working as in W^{iv}, above the critical range, gives a fine grain, but subsequent cold work at just above atmospheric temperature gives a very much distorted structure.

It may be well to note in this connection that recent work by M. A. Grossman and others has brought out the fact that actually there may be recrystallization below the critical range of certain constituents. At approximately 675° C. the alpha grains recrystallize spontaneously; below this temperature they remain distorted.

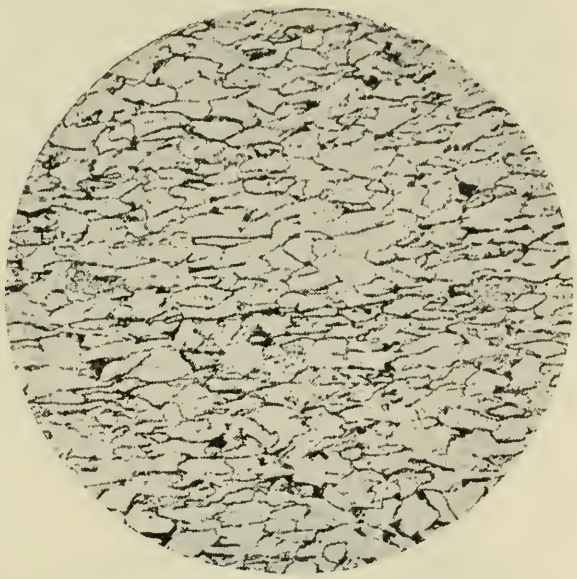

FIG. 225. Low-carbon steel (ferrite and pearlite). (Severely cold-worked) (× 100)

Photograph by Dr. V. O. Homerberg

730. Effect of cold work on the physical properties. As already pointed out, cold work results simply in a distortion of the existing structure. The tensile strength, elastic limit, and hardness are increased to a marked degree. The intensity of these changes increases as the temperature falls, being most marked at room temperature. It may be carried so far as to render the metal too brittle for ordinary use. The ductility, as well as the resistance to shock, is materially diminished by this treatment. The distortion due to cold work is well shown in Fig. 225.

731. Effect of hot work on the physical properties. Hot working, if it is continued down to the critical range, will give the steel the finest possible grain and impart to it many desirable properties. It will be more malleable, more ductile, will resist shock better, be softer, and have a lower tensile strength than a cold-worked piece.

HEAT TREATMENT OF STEEL

732. General. One of the marked properties of steel is that of having its structure and many of its physical properties greatly changed by thermal treatment. The rate of heating, the rate of cooling, the temperature reached, and the atmosphere in which the heating takes place, all have an influence on the final result. For example, by heat treatment alone we can increase the hardness, the tensile strength, or the elastic limit of eutectoid steel by as much as 100 per cent. We can get a steel which is soft, ductile, and malleable or one that is very strong, glass hard, and brittle.

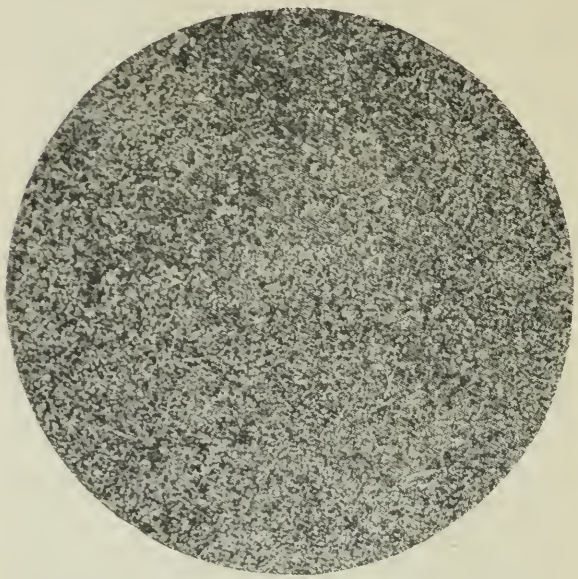

FIG. 226. Sorbite (0.35 per cent C). (× 250)

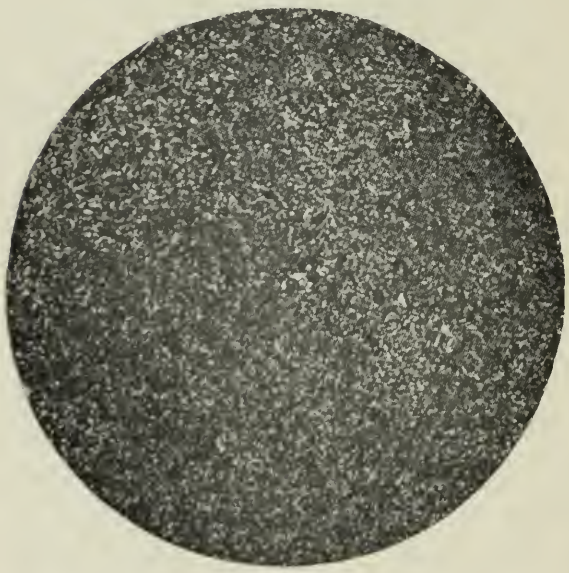

FIG. 227. Troostite (0.85 per cent C). (× 250)
Nitol etch

733. Influence of the rate of cooling. If we take a piece of eutectoid steel and cool it very slowly from just above the critical range, we find that at room temperature it will consist of a mass of pearlite. In this condition it will be soft, ductile, and relatively weak. If we take this same piece of steel and cool it a bit more rapidly, — in air, for example, — we get a different and yet characteristic structure which we call sorbite. Such a structure is shown in Fig. 226. If we cool the piece still

more rapidly, — let us say by quenching in oil, — we get still another structure, troostite, which is shown in Figs. 227 and 228. Finally, if we cool the piece as rapidly as possible by quenching in water, we get a structure called martensite, shown in Figs. 229 and 230. Theoretically austenite should result, but the decomposition of the solid solution into the new structure, martensite, is so rapid that unless special precautions are observed or retarding agents added all the austenite will change over into martensite. One property which varies progressively in these different structures is that of hardness, as indicated below:

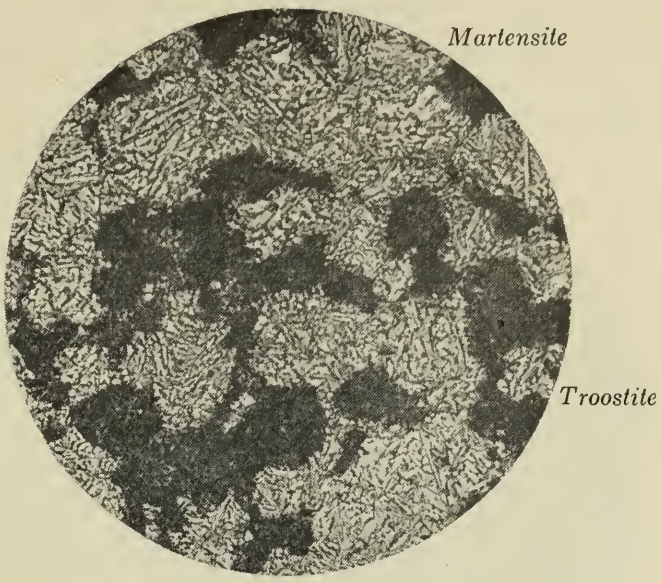

FIG. 228. Martensite and troosite. (× 500)
Nitol etch. (Photograph by Dr. V. O. Homerberg)

	BRINELL HARDNESS
Ferrite	80
Pearlite	200
Sorbite	200–400
Troostite	400–550
Martensite . . .	600
Cementite . . .	600 (?)

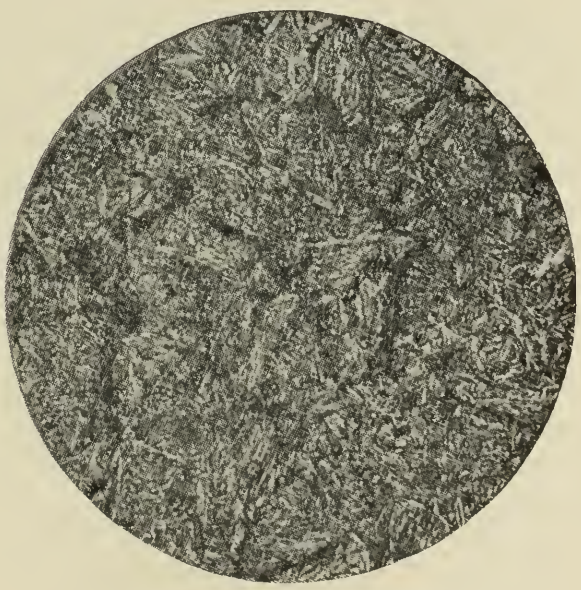

FIG. 229. Martensite. (× 500)
Nitol etch. (Photograph by Dr. V. O. Homerberg)

It is very hard, in the light of our present knowledge of these structures, to say what brings about these changes in the properties of the steel. We know that austenite

is a solid solution of C or Fe_3C in gamma iron, and that pearlite is a very fine-grained aggregate, or mosaic, of ferrite and cementite. We believe that sorbite, troostite, and martensite are steps in the decomposition of austenite into pearlite, the extent or completeness of the break-up depending upon the time or, what is just the same, the rate of cooling. A very drastic quench does not allow the decomposition to go on to any great extent, and we get martensite, while very slow cooling produces complete breakdown into the aggregate pearlite. We have already defined austenite and pearlite; let us now attempt to define (after Sauveur) these new constituents.

FIG. 230. Martensite. (× 1250)

Photograph by Bausch and Lomb Optical Company

Martensite is an early stage in the transformation of austenite into pearlite, — probably an aggregate of austenite and troostite.

Troostite is a solid solution of C or Fe_3C in non-gamma iron (whether alpha or beta it is impossible to say at present).

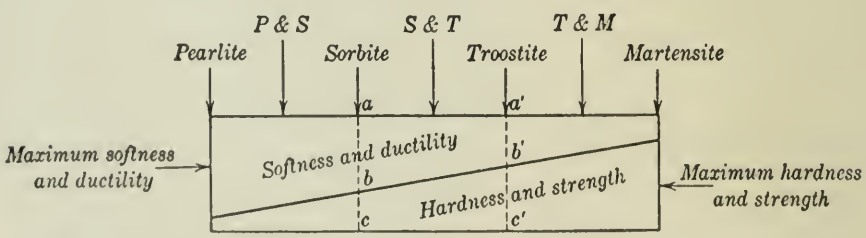

FIG. 231. Constituents of steel and their physical properties

After Sauveur

Sorbite is an uncoagulated mixture of the constituents of troostite and pearlite.

The variation of some of the physical properties with these structures can best be shown by Fig. 231.

734. Annealing. Annealing consists of slow cooling from a temperature just above the critical range. It is essentially a pearlitizing process. By such treatment we should expect to develop (1) softness; (2) ductility; (3) grain refinement; (4) grain uniformity; (5) absence of internal strains. The temperature to which the piece must be heated will depend upon the carbon content, as indicated below:

Carbon Content	Annealing Range
Less than 0.12 per cent	875°–925° C.
0.12–0.29 per cent	840°–875° C.
0.30–0.49 per cent	815°–840° C.
0.50–1.00 per cent	790°–815° C.

The length of time it must be held at this temperature will of course vary with the mass of the article being treated; a heavy plate must be annealed for a much longer time than a thin sheet. The rate of cooling will vary somewhat with the carbon content as well. Steels with less than 0.15 per cent of C may be quenched in water, thereby increasing the strength and elastic limit, and those with less than 0.20 per cent may be quenched in oil, while all high-carbon steels must be cooled very slowly in order to acquire the full benefits of this sort of treatment.

Annealing is especially valuable in rectifying the distorted structure developed under excessive cold work, — for example, in rolling and drawing. This is shown in Fig. 217. The elongated grains of Fig. 225, heated just above the critical range, have an opportunity to recrystallize, thus developing new strength and removing the strains incidental to cold work.

735. Normalizing. This is a term frequently used in the description of steels, and, unfortunately, very often loosely used. Normalizing is really a particular form of annealing, for it consists in cooling the piece in air from just above the critical range. It might just as well be called equalizing, for it is used commercially to obtain uniform structures and properties in billets, rods, rails, etc. Normalizing does not always give identical structures in differently shaped pieces. For example, such cooling might develop a pearlitic structure in a very large piece and a sorbitic one in a piece of small cross section. The important fact is that in similar pieces it will always develop the same structure and gives the consumer something on which to base any subsequent mechanical or thermal treatment.

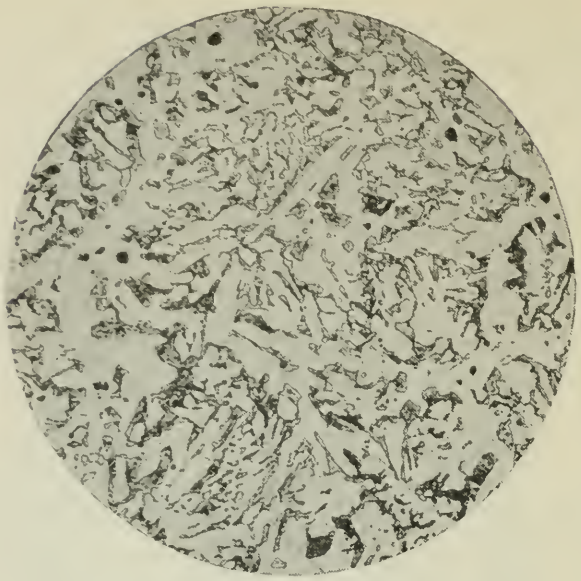

FIG. 232. Cast steel as cast. (× 100)
Nitol etch. (Photograph by Dr. V. O. Homerberg)

Steel castings are very apt to develop ingotism (very coarse grain) during cooling. Particularly is this true if they are large cross sections. The refinement of the grain through annealing is well shown in Figs. 232 and 233.

736. Hardening. This consists in heating the piece of steel to just above the critical range and quenching it, either in oil or in water, depending upon the composition of the steel. One must not go too much above the critical range, or subsequent cooling will develop a coarse grain and a correspondingly brittle structure. Ordinarily the aim is to go from 20 to 50° C. above Ac_1 in eutectoid and hypereutectoid steels or above Ac_{3-2} in hypo-eutectoid steels. Such hardening treatment tends to develop in the steel (1) maximum refinement of the grain; (2) maximum hardness; (3) maximum tensile strength; (4) minimum ductility; (5) internal stresses.

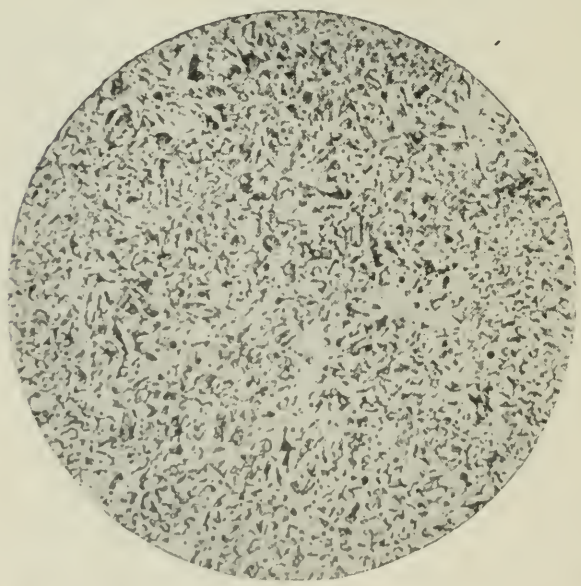

FIG. 233. Cast steel normalized. (× 100)
Nitol etch. (Photograph by Dr. V. O. Homerberg)

737. Tempering. While they possess extreme hardness, steels which have been quenched are ordinarily not capable of being worked or used for most purposes. While they possess great

tensile strength, they are not ductile and may be so brittle as to fracture with a light blow of a hammer. The tempering operation is really an attempt at compromise; that is, the metallurgist seeks by further thermal treatment to develop ductility and resistance to shock by sacrificing a little of the strength and hardness of the piece.

The reaction

austenite ⟶ martensite ⟶ troostite ⟶ sorbite ⟶ pearlite

is in a sense a reversible one. That is, while the abstraction of heat may bring about the formation of a certain constituent, the application of heat to an already *hardened* (this is important) steel may develop this same constituent. On the temperature reached in heating will depend the character of the constituent. This tempering consists in heating an already hardened steel to some point below the critical range in order to bring about a change into sorbite or troostite or a mixture of the two. We cannot by tempering develop pearlite; in order to reproduce this structure we must heat the piece above the critical range and cool slowly, and this of course is not tempering but annealing.

The changes brought about in tempering are gradual ones. If we reheat a piece of martensitic steel, the martensite begins to change over into troostite; at a temperature of 400° C. the change is complete and the steel is entirely troostite. On further heating, sorbite begins to develop; at 600° C. the change is complete. On still further heating, the sorbite persists until the critical range is reached, when the sorbite changes into austenite. The rate of cooling from a tempering operation, once the desired constituent has been obtained, does not appear to affect the structure of the piece.

738. Spheroidizing. This is a special form of heat treatment employed in certain high-carbon steels. In the discussion of the Fe-C equilibrium diagram it was pointed out that in the slow cooling of hypereutectoid steels the excess cementite is rejected to the grain boundaries. This structure is particularly undesirable when the piece is to be machined, since the relatively large particles of hard cementite tend to dull the edge of the cutting tool. This condition of cementite is not a stable one. If the piece is held for a long time just below the critical range,

or bobbed up and down just at the critical range, the lamellar cementite (both excess and pearlitic) will be converted into rounded particles embedded in a matrix of ferrite, — that is, spheroidized. Cementite in this condition can be likened to bullets embedded in putty. While the bullets themselves may be hard, any deformation of the mass as a whole will move the bullets around in the putty and eventually remove a piece of it. The tool, then, in cutting spheroidized material, has a much longer life. After machining, this structure, by heat treatment, can be replaced by any other structure.

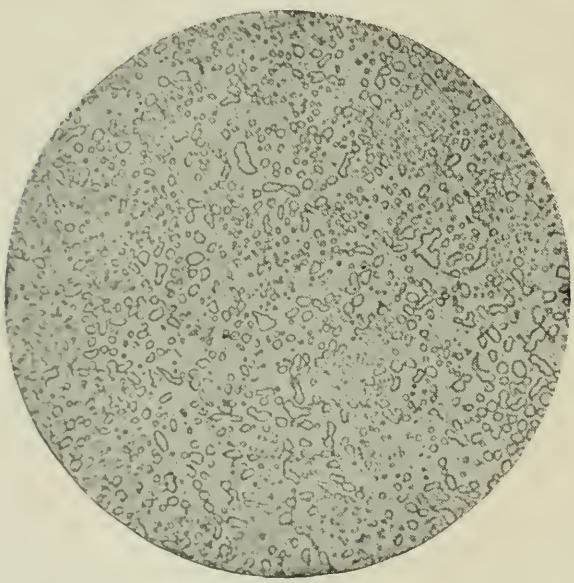

FIG. 234. Spheroidized steel. (× 500)
Nitol etch. (Photograph by Dr. V. O. Homerberg)

739. Case-hardening. Very often it is desirable to have a metal which is hard and at the same time possesses considerable ductility and resistance to shock. For example, in a cam shaft we should like to have a hard-wearing surface to withstand the rubbing of the cams, and at the same time a material that will stand up under the impact and pressure of the valve rods. We can often get such a desirable combination of properties by the process of case-hardening. By this treatment we get a hard surface (the case) and a ductile interior (the core).

We have already discussed, from a practical standpoint, the cementation of wrought iron to produce various grades of plain carbon steel. For a number of years it was held that this cementation consists simply in the bodily transfer of the carbon from the charcoal or coke into the metal. Such a theory is incompatible with present-day knowledge. We now believe that it is the gas or gases liberated during the carburizing period that effect the transfer of the carbon. Carbon monoxide and cyanogen compounds appear to be most effective. The former is derived from the incomplete combustion of the carbon, the

latter from the decomposition of potassium cyanide or ferrocyanide formed by the union of C and N at the elevated temperatures employed. The reactions involved are

$$2\,CO + 3\,Fe = Fe_3C + CO_2$$

and the immediate reduction of the CO_2, thus,

$$CO_2 + C = 2\,CO,$$

to be used over again.

The carburizing material may be solid, liquid, or gaseous, the former being by far the most common. Charcoal, crushed bone, barium carbonate, beet-sugar pulp, potassium cyanide, and charred leather or horn are common carburizing agents. A widely employed mixture is $BaCO_3$ (40 per cent) and charcoal (60 per cent). The cyanogen compounds give quicker, superficial cases but soon lose their effectiveness.

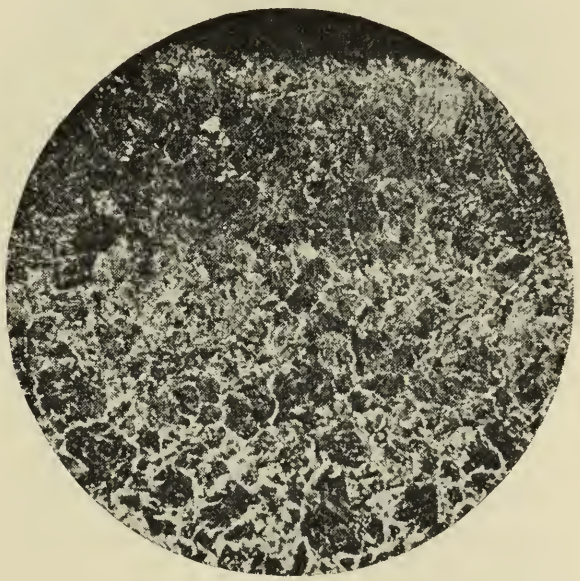

FIG. 235. Case-hardened steel. (× 25)
Nitol etch. (Photograph by Dr. V. O. Homerberg)

It is evident that the temperatures employed must be just above the critical range in order to get the iron into the gamma form so that it may the more readily absorb the Fe_3C as it is formed. The higher the temperature the faster will be the absorption and the deeper the penetration. On the other hand, subsequent cooling, if the temperature is too high, will yield a coarse grain. Most case-hardening operations are conducted at temperatures between 900° and 950° C. Ordinarily, too, an effort is made to keep the carbon content of the case below 0.90 per cent, in order to develop the greatest hardening power and avoid danger of cracking when quenched.

The structure of the case-hardened piece is shown in Fig. 235. One can easily distinguish the high-carbon case, with the large

amount of pearlite, from the low-carbon core, with the large amount of ferrite.

740. Malleable cast iron. Malleable cast iron is at best a misnomer, for the cast iron produced by the malleableizing treatment, while it is certainly more resistant to shock than ordinary cast iron, is far from being malleable in the true sense of the term. It finds wide use for such purposes as the manufacture of pipe fittings, cheap tools, and hardware.

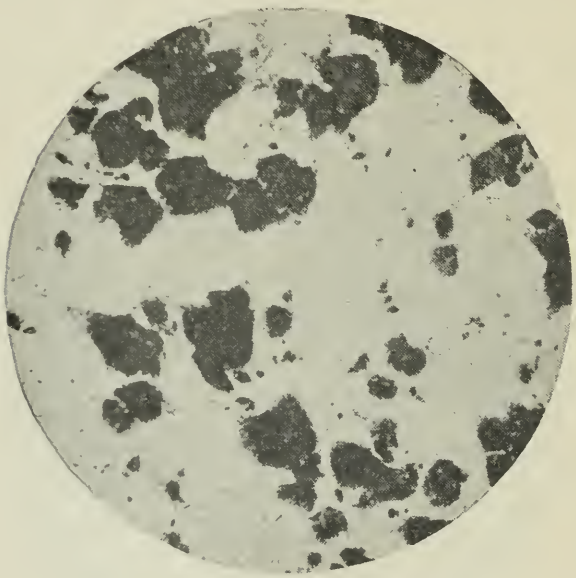

FIG. 236. Malleable cast iron. (× 100)
Nitol etch. (Photograph by Dr. V. O. Homerberg)

It was pointed out in the discussion of the Fe-C equilibrium diagram that Fe_3C is an unstable compound; that prolonged heating above the critical range tends to decompose it thus:

$$Fe_3C = 3\ Fe + C.$$

The carbon which separates out in this way is different from the carbon of ordinary cast iron both in its appearance and in the properties which it imparts to the iron. A typical malleable iron is shown in Fig. 236. The large black specks are temper carbon resulting from the decomposition of the Fe_3C present in the original casting.

The original castings are what are termed hard castings in that they are almost always of white cast iron. The reason for this is apparent. Since the desirable properties of the casting are obtained by the presence of temper carbon, not graphite, it is desirable to have as little graphite and as much cementite as possible present. Ordinarily the percentage of carbon will range from 2.00 to 3.00. The formation of temper carbon is favored by (1) the presence of much cementite; (2) high silicon and low manganese or sulphur; (3) high temperature; (4) long exposure at this temperature. Even though the silicon does favor the break-up of the cementite, there is a limit to the

amount that can be present, owing to the fact that it is impossible to make white-iron castings in the presence of much silicon. The amount will vary with the mass of the piece, from 0.30 per cent in large castings to 1.25 per cent in small ones.

The castings are placed in an annealing box and packed in some suitable material. This may be (1) oxidizing or (2) non-oxidizing in character, depending upon the kind of malleable castings desired. Complete elimination of the carbon, thus,

$$3\ Fe_3C + Fe_2O_3 = 11\ Fe + 3\ CO,$$

is accelerated by the presence of an oxidizing material like Fe_2O_3, while the simple decomposition of the cementite into temper carbon and ferrite is favored by the presence of an inert, or nonoxidizing, packing. For a long time it was believed that almost complete removal of the carbon was necessary in order to produce the most desirable properties, but at the present time a great deal of malleableizing is carried out with a pack which removes little of the carbon, depending chiefly upon the graphitizing of the cementite to confer the small amount of malleability on the piece. Iron ore, mill scale, and puddle cinder are some of the common packing materials used. On the degree of removal of the carbon will depend the kind of casting we turn out. If we use a highly oxidizing pack and burn out most of the carbon we get a so-called white-heart casting, while if graphitizing alone is carried out we get a black-heart casting. Of course, even in the black-heart casting there is usually a thin skin or decarburized rim from which all the carbon has been removed.

In annealing for white-heart castings they are held at a temperature of from 800° to 900° C. for from four to five days. Since the oxidation of the carbon necessarily requires a long time it follows that only white-heart castings of small size are made, usually not over $\frac{1}{2}$ inch in thickness. In annealing for black-heart castings they are held between 700° and 800° C. for from two and one-half to three and one-half days, the oxidation of the carbon being of secondary importance. In either case the cooling from the annealing temperature to 675° C. should be very slow, occupying not less than forty-eight hours. A typical annealing cycle would consist of approximately one hundred and fifty-five hours.

ALLOY STEELS

741. General. In the sections on metallography we have discussed the properties of the plain carbon steels. While the desirable qualities of these steels are due, to a great extent, to the presence of varying amounts of carbon, we find that other elements also play their parts. For example, our so-called plain carbon steels contain from 0.30 to 0.80 per cent of Mn, from 0.10 to 0.35 per cent of Si, a maximum of 0.05 per cent of S, and a maximum of 0.045 per cent of P. So general and beneficial is the use of these small amounts of other elements that we really ought to divide our steels into three classes, as follows: (1) plain carbon steels; (2) alloy-treated steels; (3) alloy steels.

Plain carbon steels have already been defined. Alloy-treated steels are those to which one or more elements have been added for curative purposes, but which do not contain enough of the element or elements to cause any material change in their properties. They are usually superior to plain carbon steels because of more nearly perfect deoxidation and degasification. Alloy steels are those to which enough of one or more elements has been added to change the properties of the steel materially. It is with the last class of steels that we are now concerned.

742. Effect of the addition. It is very difficult to make a definite statement concerning the effect of any one element on the steel, for the presence of small amounts of another element and heat treatment have a profound effect upon its properties. Among the common effects of alloy additions are the following:

1. The tensile strength may be increased.
2. The critical points may be raised or lowered or entirely disappear.
3. The speed of quenching for maximum hardness may be decreased.
4. The toughness may be increased.
5. Other physical properties, such as magnetic permeability and the coefficient of expansion, may be changed.
6. The resistance to corrosion may be increased.

743. Classification of alloy steels. In a general way the alloy steels may be divided into four classes according to the structure developed on air cooling:

1. Those steels which become pearlitic or sorbitic on air cool-

ing. Such steels are often used for structural purposes, since on heat treatment they yield higher tensile strength, elastic limit, and hardness combined with ductility.

2. Those steels which become troostitic or martensitic after air cooling. These steels are air-hardening and thus eliminate the danger of cracking in the quenching operation. In the martensitic condition they are much more stable than ordinary steels, retaining their hardness at higher temperatures.

3. Those steels which remain untransformed, — that is, in the austenitic condition. Such steels are very resistant to abrasion.

4. Those steels which contain more than a normal amount of free carbides (cementitic steels). The most valuable property of these steels is the power which they possess, when the carbides are dissolved in the austenitic matrix, of retaining their hardness when heated to temperatures that would soften ordinary steels.

Nickel Steels

744. General effect of nickel. Nickel as an alloying agent covers a greater range than almost any other element. Nickel steels in common use vary from as little as 0.5 per cent Ni up to permalloy, which contains 78.2 per cent Ni and only 21.3 per cent Fe.

Nickel dissolves in all proportions in both gamma and alpha iron. Ordinarily it does not form a carbide. The nickel cannot be detected microscopically, being present in the ferrite of the steel. Nickel lowers the critical points both on heating and on cooling. It tends to develop a finer grain size. As indicated in Fig. 237 the nickel steels, depending upon the Ni and C content, may be austenitic, martensitic, or pearlitic.

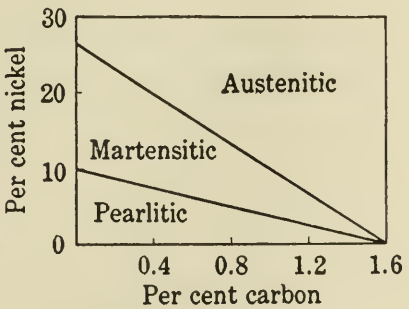

Fig. 237. Constitutional diagram of nickel steels

745. Pearlitic nickel steels. These are by far the most important of the nickel steels, for they find a wide use as structural material. Usually the nickel content is less than 5 per cent, since the higher-nickel steels are difficult to work. In these steels the general effect of the nickel is to increase the strength without causing a corresponding decrease in the ductility or hardness.

Steels containing from 0.5 to 1.5 per cent of Ni are chiefly used for case-hardening, since the core produced is tougher and the case harder, after an oil quench, than plain carbon steel.

Steels containing 3.5 per cent of Ni are used in bridges, locomotive and engine parts, special bolts, studs, and castings. This is probably the most generally used of the nickel steels.

746. Martensitic nickel steels. Steels with a higher content than 5 per cent of Ni are not generally used. They are all martensitic and are of course very difficult to work or machine.

747. Austenitic nickel steels. While steels above 20 per cent Ni are not used to the same extent as the lower-nickel steels, since they are in the austenitic condition, they have some very valuable properties. They are nonmagnetic and have very low coefficients of expansion and remarkable resistance to high temperatures. The alloy invar, for example, has a coefficient of expansion of only 2.01×10^{-6} (20° C.–100° C.). Steels with from 25 to 35 per cent of Ni are extensively used for valves, seamless tubes, and as resistors in electric furnaces.

Manganese Steels

748. General effects of manganese. The manganese content of commercial steels ranges from a few hundredths of 1 per cent up to about 15 per cent. The beneficial effects of manganese in deoxidizing and desulphurizing steels have already been described, as well as the effects of small amounts of the element on plain carbon steels. Manganese forms solid solutions with both gamma and alpha iron. In the presence of carbon Mn_3C is formed, which dissolves in gamma iron at high temperatures. It is natural to expect, then, that manganese steels, on slow cooling from above the critical range, would be first pearlitic, then martensitic, and finally austenitic, as indicated in Fig. 238. In general Mn tends to increase the strength and hardening power and to decrease the toughness.

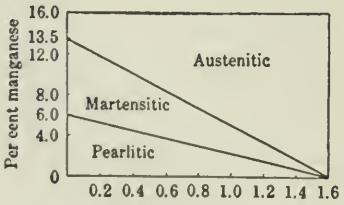

Fig. 238. Constitutional diagram of manganese steels

749. Pearlitic and martensitic manganese steels. These steels are used very little today. The former are seldom met with, because the low-carbon steels are difficult to make and many steel

manufacturers believe that such steels are brittle. The latter are not used because of their hardness and brittleness, which render them difficult to work.

750. Austenitic manganese steels. These are of considerable industrial importance. The common variety contains from 10 to 15 per cent of Mn and from 1 to 1.5 per cent of C. It is often called Hadfield steel, from the name of its inventor. These steels, in either the quenched or the slowly cooled condition, are austenitic. Without heat treatment they are rather brittle and have little ductility. The usual heat treatment consists in heating above 990° C. (in order to dissolve the carbides) and quenching in water.

High-manganese steels are used a great deal where resistance to wear and abrasion is important, as in the manufacture of excavating machinery, crushers, grinders, and railroad switches. They are also nonmagnetic in character. They possess two distinct disadvantages: (1) After heat treatment the elastic limit is low and the steel tends to flow under load or impact. (2) Owing to its great hardness it cannot be machined or formed.

Chromium Steels

751. General effects of chromium. This metal dissolves in molten iron and is retained in solid solution in both gamma and alpha iron. In the presence of carbon it forms a carbide, the exact composition of which is still under debate. This carbide seems to be more stable than Fe_3C, so that the effect of chromium is to increase the hardening power of the carbon in the steel. Chromium raises the *Ac* point and lowers the *Ar* point. It increases the elastic limit and strength, while it decreases the ductility. Hardening penetrates deeper on chromium steels than on plain carbon steels of the same carbon content. While sometimes used alone, it more commonly appears in combination with some other alloying agent such as Ni, V, W, or Mo. The constitutional diagram after slow cooling from above the critical range is given in Fig. 239.

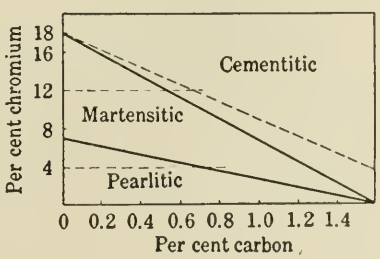

Fig. 239. Constitutional diagram of chromium steels

752. Pearlitic chromium steels. These, the low-carbon steels, are the most important of the simple chromium steels. They are used a great deal for the case-hardening of parts requiring an extremely hard-wearing surface, — for example, in the manufacture of special gears, pins, shafts, balls, and ball races.

The medium-carbon steels are used in the manufacture of parts requiring great strength and toughness, such as steering knuckles, shafts, and axles, as well as shear blades and dies.

The higher-carbon steels, from 0.90 to 1.30 per cent C, are used for their great hardness in the manufacture of tools, files, and ball and roller bearings.

753. Martensitic chromium steels. These steels are most important for their stainless properties. Many such steels have been patented, but the usual composition is in the neighborhood of from 12 to 14 per cent of Cr and from 0.25 to 0.40 per cent of C. This stainless steel finds wide use in cutlery and containers, since it withstands the action of the atmosphere, sea water, dilute acids, fruit and vegetable juices, etc. It is to be noted that these stainless properties are not fully developed until the material has been heat-treated. This consists in heating to from 940° to 1040° C., for the purpose of getting the carbides into solution, followed by quenching in oil. Hardness and strength are usually increased by tempering at about 530° C.

754. Cementitic chromium steels. These steels consist of martensite with excess cementite embedded in it. They are used principally for materials which must resist corrosion and high temperatures, — for example, the resistor elements in electric furnaces.

Vanadium Steels

755. General effects. Vanadium forms solid solutions with both gamma and alpha iron. In the presence of carbon a carbide (V_4C_3) is formed. There is evidence to show that this carbide has the power to replace cementite in the pearlite, forming what we may call vanadium pearlite. When present in amounts not exceeding 0.2 per cent, vanadium raises both the Ar_1 and Ar_3 points. It deoxidizes the molten metal, refines the grain, and increases the strength, elastic limit, hardness,

and resistance to shock and fatigue. It enhances the valuable properties imparted to steel by chromium. It is seldom used alone, but usually in combination with nickel or chromium.

Tungsten Steels

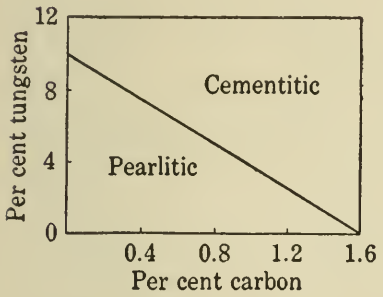

Fig. 240. Constitutional diagram of tungsten steels

756. General effects. Tungsten dissolves in gamma iron and remains dissolved in alpha iron on cooling to room temperature. In the presence of carbon it forms carbides, the exact formulas of which are still a debated question. If the carbides are kept in solution this element tends to refine the grain and improve the cutting hardness of the alloy. Since air cooling usually accomplishes this, tungsten steels are often referred to as self-hardening. Tungsten is seldom used alone in steel, but usually in combination with two or more alloying agents.

Silicon Steels

757. General effects. Silicon unites with iron to form the silicide FeSi, which forms solid solutions with both gamma and alpha iron. The constitutional diagram for silicon steels is shown in Fig. 241. It will be seen that the structure is dependent entirely on the silicon content. Silicon increases the elastic limit, coarsens the grain, and decreases the ductility of the steel. It decreases the solubility of carbon in iron, thus promoting graphitization. Silicon steels are used a great deal in the electrical industry, for the addition of this element has notable effects on the magnetic and electrical properties of the metal. It increases the resistance, reduces coercive force, and increases permeability

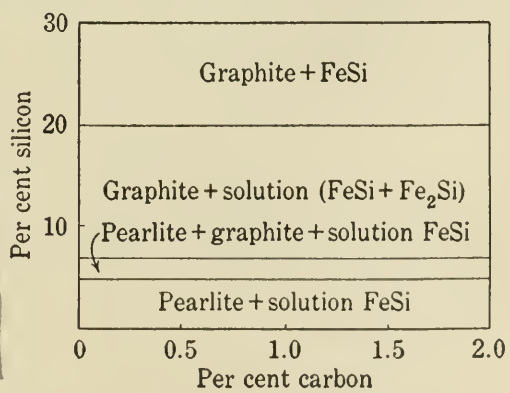

Fig. 241. Fe-Si equilibrium diagram

below saturation. It increases the resistance of iron to most acids. Silicon spring steel is very popular. None of these steels contain more than 5 per cent of Si.

Copper Steels

758. General effects. Copper forms solid solutions with gamma iron and with alpha iron. It does not form carbides in the presence of carbon. The addition of from 0.15 to 0.30 per cent of Cu increases the resistance of mild steel to atmospheric corrosion. In amounts larger than 0.5 per cent it tends to make the alloy red-short.

Molybdenum Steels

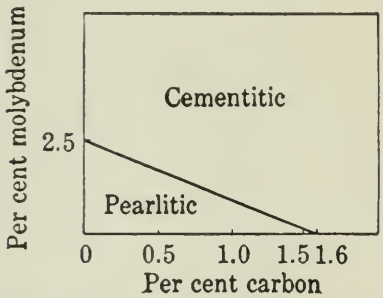

Fig. 242. Constitutional diagram of molybdenum steels

759. General effects. This metal dissolves in both gamma and alpha iron. In the presence of carbon it forms a carbide of as yet undetermined composition. The constitutional diagram is given in Fig. 242. This element acts in a manner similar to tungsten. Until recently the element was not extensively used, on account of its high price and the belief among manufacturers that molybdenum steels were unreliable and inclined to be seamy. In the last few years there has been a decided increase in its use in combination with other elements.

Chromium-Vanadium Steels

760. General effects. Steels within the following composition range are in very common use today:

Chromium	0.80–1.10 per cent*
Vanadium	0.15–0.20 per cent
Manganese	0.50–0.80 per cent
Sulphur	0.04 maximum
Phosphorus	0.04 maximum
Carbon	Varying amounts, depending upon use

These steels have a much finer grain than the corresponding plain carbon steels. As with most alloy steels, the full value of

* See *Transactions of the American Society for Steel-Treating*, September, 1927.

the alloying agents is obtained only after heat treatment. These steels are also extensively used in case-hardening, since they appear to absorb carbon much more rapidly and uniformly than the plain carbon steels. They also find wide use in gears, shafts, and parts requiring great toughness and strength, in spring steel, and in tools.

Nickel-Chromium Steels

761. General effects. We should expect these steels to show the beneficial effects of both the alloying agents, and as a matter of fact they do. These steels are used whenever the highest strength, toughness, and hardening power are desired, particularly in the automotive field. They may be divided into classes according to their carbon content.

762. Low-carbon steels. Steels such as S.A.E.* 3115 and 3120 are used primarily for case-hardening. They have the advantage over plain carbon steels that the case-hardened articles produced will have greater strength, toughness, and surface hardness.

763. Medium-carbon steels. These steels are used in the manufacture of forgings in which great strength and toughness are required, such as automobile steering mechanisms, connecting rods, gears, and bolts. They must be heat-treated.

764. High-nickel-chromium alloys. These are really not steels at all, for they are used mostly for their resistance to heat, corrosion, and oxidation. They range in composition from about 20 per cent Ni + Cr up to alloys consisting entirely of these two elements. A few examples (in per cents) are given below:

	Ni	Cr	C	Si
	Per Cent	*Per Cent*	*Per Cent*	*Per Cent*
Alloy 1	22.0	5.5	0.15	1.25
Alloy 2	36.0	27.5	0.70	3.25
Alloy 3	60.0	16.0	—	—
Alloy 4	85.0	15.0	—	—

They are used for electrical resistors or heatings elements, thermocouple wires, carburizing pots and boxes, pyrometer protecting tubes, and general furnace parts. Both castings and forgings may be made from these alloys.

*Society of Automotive Engineers.

High-Speed Steels

765. General. It is impossible to generalize on the effects of the different elements on these steels, for they are very complex alloys. While they are essentially alloys of iron, carbon, tungsten, and chromium, many of them contain also notable amounts of Va, Si, Mn, Co, and Mo. Accordingly we may have the following compounds existing in high-speed steel: Fe_3C, CrC, WC, Fe_3W, and V_4C_3. These carbides may crystallize out of solution, may be retained in solution as austenite, or may be converted, through partial transformation, into martensite. The valuable property of these steels is their ability to retain their hardness when heated well above the critical range. Modern high-speed steels are included in the following range of compositions:

	Per Cent
Carbon	0.30–0.75
Tungsten	12–20
Chromium	4–7
Vanadium	1
Manganese	0.40

766. Steel nomenclature. The S.A.E. steel specifications are frequently used in classifying steels, even though they are not intended for automotive use. A numeral index system is used which makes it possible to use these specification numerals on shop drawings or to use the numbers in conversation without referring to the cumbersome analysis. The first figure of such a number indicates the class to which the steel belongs. The basic numerals are as follows:

Carbon steels	1
Nickel steels	2
Nickel-chromium steels	3
Molybdenum steels	4
Chromium steels	5
Chromium-vanadium steels	6
Tungsten steels	7
Silicon-manganese steels	9

The second figure (in alloy steels) indicates the approximate percentage of the principal alloying agent. The last two figures indicate the average carbon content. A few examples will show better the principle of this system:

Plain Carbon Steels

Steel	Carbon (Range)	Manganese (Range)	Phosphorus (Maximum)	Sulphur (Maximum)
	Per Cent	*Per Cent*	*Per Cent*	*Per Cent*
No. 1010	0.05–0.15	0.30–0.60	0.045	0.05
No. 1040	0.35–0.45	0.50–0.80	0.045	0.05
No. 1050	0.45–0.55	0.50–0.80	0.045	0.05

Nickel Steels

Steel	Carbon (Range)	Manganese (Range)	Phosphorus (Maximum)	Sulphur (Maximum)	Nickel (Range)
	Per Cent	*Per Cent*	*Per Cent*	*Per Cent*	*Per Cent*
No. 2315	0.10–0.20	0.30–0.60	0.04	0.045	3.25–3.75
No. 2350	0.45–0.55	0.50–0.80	0.04	0.045	3.25–3.75

Nickel-Chromium Steels

Steel	Carbon (Range)	Manganese (Range)	Phosphorus (Maximum)	Sulphur (Maximum)	Nickel (Range)	Chromium (Range)
	Per Cent	*Per Cent*	*Per Cent*	*Per Cent*	*Per Cent*	*Per Cent*
No. 3120	0.15–0.25	0.30–0.60	0.04	0.045	1.00–1.50	0.45–0.75
No. 3340	0.35–0.45	0.30–0.60	0.04	0.04	3.25–3.75	1.25–1.75
No. 3450	0.45–0.55	0.45–0.75	0.04	0.04	2.75–3.25	0.60–0.95

Chromium Steels

Steel	Carbon (Range)	Manganese (Range)	Phosphorus (Maximum)	Sulphur (Maximum)	Chromium (Range)
	Per Cent	*Per Cent*	*Per Cent*	*Per Cent*	*Per Cent*
No. 5120	0.15–0.25	0.30–0.60	0.04	0.045	0.60–0.90
No. 52100	0.95–1.10	0.20–0.50	0.03	0.03	1.20–1.50

Chromium-Vanadium Steels

Steel	Carbon (Range)	Manganese (Range)	Phosphorus (Maximum)	Sulphur (Maximum)	Chromium (Range)	Vanadium
	Per Cent	*Per Cent*	*Per Cent*	*Per Cent*	*Per Cent*	*Per Cent*
No. 6125	0.20–0.30	0.50–0.80	0.04	0.04	0.80–1.10	0.18
No. 6150	0.45–0.55	0.50–0.80	0.04	0.04	0.80–1.10	0.18

TUNGSTEN STEELS

STEEL	CARBON (RANGE)	MANGANESE (RANGE)	PHOSPHORUS (MAXIMUM)	SULPHUR (MAXIMUM)	CHROMIUM (RANGE)	TUNGSTEN (RANGE)
	Per Cent	*Per Cent*	*Per Cent*	*Per Cent*	*Per Cent*	*Per Cent*
No. 71360	0.50–0.70	0.30	0.035	0.035	3.00–4.00	12.00–15.00
No. 7260	0.50–0.70	0.30	0.035	0.035	0.50–1.00	1.50– 2.00

SILICON-MANGANESE STEEL

STEEL	CARBON (RANGE)	MANGANESE (RANGE)	PHOSPHORUS (MAXIMUM)	SULPHUR (MAXIMUM)	SILICON (RANGE)
	Per Cent	*Per Cent*	*Per Cent*	*Per Cent*	*Per Cent*
No. 9250	0.45–0.55	0.60–0.90	0.045	0.045	1.80–2.20

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CHAPTER XVII

SAMPLING AND SCHEDULES

RECEIVING AND SAMPLING OF ORES AND METALS

767. General. The operator of a smelter or refinery buys ores or metals as a miller buys grain or as a packer buys beef. If he purchases a lead-silver-gold ore, for example, he must be able to determine accurately the amount of these metals in the ore and pay the shipper for them, deducting a charge for the smelting operation. He must then be able to reduce this ore, recover all these metals, and make a profit on the operation. If his sampling is inaccurate or his processes of reduction and refining are faulty, he is bound to lose. Smelting is an operation that cannot be conducted efficiently on a small scale, and owing to the large amounts of capital involved in the erection and operation of large plants it is seldom that the mine owner is warranted in erecting his own plant. More often he sells his ore to a centrally located plant called a customs smelter. These smelters are located at strategic points throughout the country. The smelter at Tacoma treats ores from Alaska; that at Trail, British Columbia, serves the mining districts of western Canada; the Bunker Hill and Sullivan Smelter treats ores from Idaho, Washington, and Montana; a number of smelters in Nevada, Arizona, and Texas serve the Southwest. Ordinarily a smelter treats only one ore, let us say a copper, lead, or zinc ore. A few, like the Trail smelter or that at Leadville, Colorado, produce as high as six metals.

768. Receiving and weighing. The ore is usually sent to the smelter in bulk or in sacks. As a rule only high-grade ore is ever sacked. Whatever the container may be, the weight of it is deducted and the shipper is paid for the net weight of the ore. A moisture sample is taken during the unloading of the ore, and another just after the ore is weighed, in order to determine the dry weight of the ore. All assays are based on

thoroughly dried samples; so the purchaser must know the dry weight of the ore in order to effect a settlement. It is important that this sample be taken with considerable care, for often, particularly with concentrates, the moisture content is high. Furthermore, the moisture is not evenly distributed through the material. If a grab sample is taken at random from the car of material, it may vary as much as 10 per cent from the true moisture content. All subsequent calculations based on the weight of the ore would be off by a similar amount. It affects the shipper as well as the purchaser. If the moisture sample is too low, the operator of the smelter will pay for more metal than is actually in the ore; if it is too high, the shipper will not be paid for all his metal. Since each is so vitally interested, both are represented when either the moisture sample or the assay sample is taken. The smelter usually does this sampling, the shipper employing a representative to oversee the operation, much as he would employ an attorney to represent him in court. Sometimes the smelter pays for unloading; sometimes the shipper assumes the charge. Often there is an extra charge for the unloading of material containing more than a certain stipulated percentage of moisture or for frozen material.

The moisture sample is best taken from bulk shipments by digging holes or driving a pipe into the ore at scattered points over the surface and taking small portions from every hole. If the material is in sacks, a small handful is taken from each sack as it is emptied into the bin or onto the sampling platform. These samples are placed in a hermetically sealed can and sent to the laboratory for a moisture determination. The ore is then ready for the final sampling, which may be done either by hand or mechanically. It is seldom that the moisture sample is also used as an assay sample.

769. **Hand sampling.** *Fractional selection* and *coning and quartering* are the commonest methods of hand sampling. The first consists of reserving every second or fourth shovelful as the car is unloaded, or every second or fourth sack if the material is in sacks. This is piled to one side and then sampled in a like manner until the final pile amounts to only a few hundred pounds. This may be taken down to a sample of a few pounds in weight by coning and quartering, with a split shovel or a Jones riffle.

In coning and quartering, the ore is crushed and then shoveled into a conical heap. The workman is careful to throw each shovelful exactly on the point of this conical heap. Sometimes the ore is piled around an iron bar in order to be sure of this. With a shovel or straightedge the cone is flattened out, as indicated in Fig. 243, until the ore is only a few inches in depth. It is then divided by diameters into four equal portions, two opposite ones (I and III) being reserved as a sample, and the others rejected. This sample is then crushed again, and the process is repeated, possibly several times, until a sample of only a few pounds in weight is obtained. If the work is carefully carried out, this sample will accurately represent the original ore in chemical composition. This sample is then sent to the laboratory, where it is crushed to 60 mesh or finer and taken down to a few hundred grams in weight by means of split shovels or Jones riffles.

FIG. 243. Coning and quartering

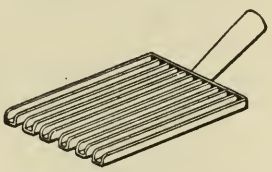

FIG. 244. A split shovel

The split shovel is illustrated in Fig. 244. It consists of a flat shovel with a number of parallel channels. Odd-numbered channels are closed at the bottom; even-numbered ones are open. When the shovel is filled and taken off the sampling table, half is left behind as a sample, and half goes with the shovel as a reject. By repeating this process several times the whole of the material to be sampled can be passed through the shovel. A more convenient method for larger samples is the Jones riffle cutter illustrated in Fig. 245. It consists of a hopper with a number of parallel riffles, or channels. The bottom of these channels is inclined, one half to one side of the cutter, the other half to the other side. Material poured into the hopper is divided into two halves, each of which accurately represents the original ore.

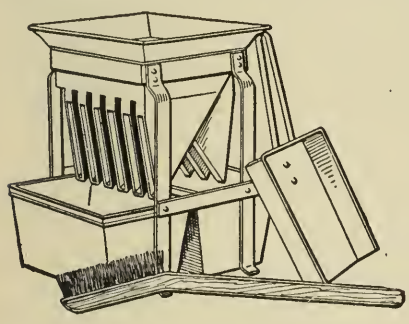

FIG. 245. The Jones riffle

Any of these methods, unless the material to be sampled is small in amount, is slow and expensive, since the material

must be handled by hand so many times. At all large plants the ore is received at a separate sampling plant before being sent to the smelter or mill, and all the operations are carried on by machinery. Mechanical sampling is cheaper, and, furthermore, since it does not involve the human element, it is more accurate. In sampling a mass of mixed minerals it is only natural for a man to pick out of it more of the valuable mineral than of the gangue, or worthless portion.

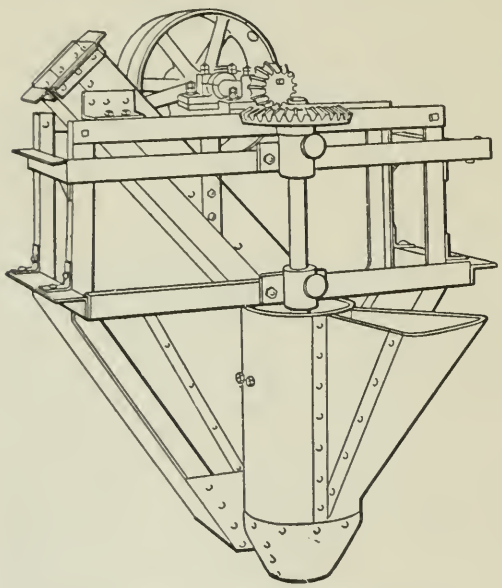

FIG. 246. The Vezin sampler

770. Mechanical sampling. Practically all the mechanical samplers are designed to take a more or less continuous sample from a falling stream of pulp or crushed ore. Theoretically, if we have such a falling stream of ore and divert the whole stream for an instant, and do this often enough, we shall have a sample which accurately represents the original ore. It is necessary to divert all the stream part of the time, not part of the stream all the time. Such a falling stream of ore has finer material on one side than on the other, and if this were to be diverted, we should probably get a sample that would be richer than the original.

The Vezin sampler is one of the most common in use. It is illustrated in Fig. 246. It consists of a hollow vertical shaft making about thirty revolutions per minute. Attached to this shaft, and emptying into it, is a segmental scoop. The area of the scoop bears such a relation to the complete circle of revolution that a fifth, sixth, or seventh of the falling stream is diverted as a sample. The ore, crushed to the proper size, enters through the inclined feed spout and is cut by the revolving scoop. The sample thus cut out falls through the central shaft and may be diverted into another sampler for further division. Usually there is a crusher between the two samplers. The reject falls into the bin below the machine, from which it

may be sent, by means of a conveyor belt, to the main ore bins of the mill or smelter. The width of the opening in the scoop must be such that the ore particles cannot lodge there and clog the opening. It is ordinarily at least six times the diameter of the largest particle in the ore stream.

771. Sampling mill. Large mills and smelters have rather elaborate sampling mills, capable of sampling carload lots of material in a few minutes' time. One of these is illustrated in Figs. 247 and 248. The railroad car empties into a hopper-bottomed bin from which the ore may be fed into a 9×15 inch Blake crusher. A 10-inch bucket elevator raises the crushed ore to the top of the building, where it is fed into No. 1 sampler. One fifth of the stream is cut out as a sample and then passes through a 7×9 inch Dodge crusher, in which it is reduced still further in size. This crushed product is fed to No. 2 sampler, where a fifth is cut out and crushed in a set of 24×14 inch rolls. This crushed product is passed through No. 3 sampler, and the sample from this is crushed in $12\frac{1}{2} \times 12$ inch rolls to about $\frac{1}{4}$ inch in size. In the sample room, located at the bottom of the sampling plant, this sample, amounting to perhaps 100 pounds for the entire car of ore, is worked down by the hand methods already described to a small assay sample. The reject from No. 1 sampler, amounting to 80 per cent of the original lot, is dropped through a chute into a car waiting on the track below. The rejects from the succeeding samplers may be elevated by small bucket elevators and loaded in the same way or allowed to fall on the ground outside of the mill and shoveled into the car.

Ordinarily three assay samples, each weighing a few hundred grams, are taken from each lot of ore. One is given to the representative of the shipper in order that he may analyze it and check against the smelter results. The second is sent to the smelter laboratory, and it is on this sample that the settlement for the entire shipment of ore is made. The third is called the umpire sample and is stored in the vaults of the smelter until the whole transaction is completed to the satisfaction of all concerned. If the shipper should be dissatisfied with the results of the smelter laboratory, he is privileged to send this umpire sample to a chemist who has been agreed upon by this shipper and the smelter. There are certain allowances specified

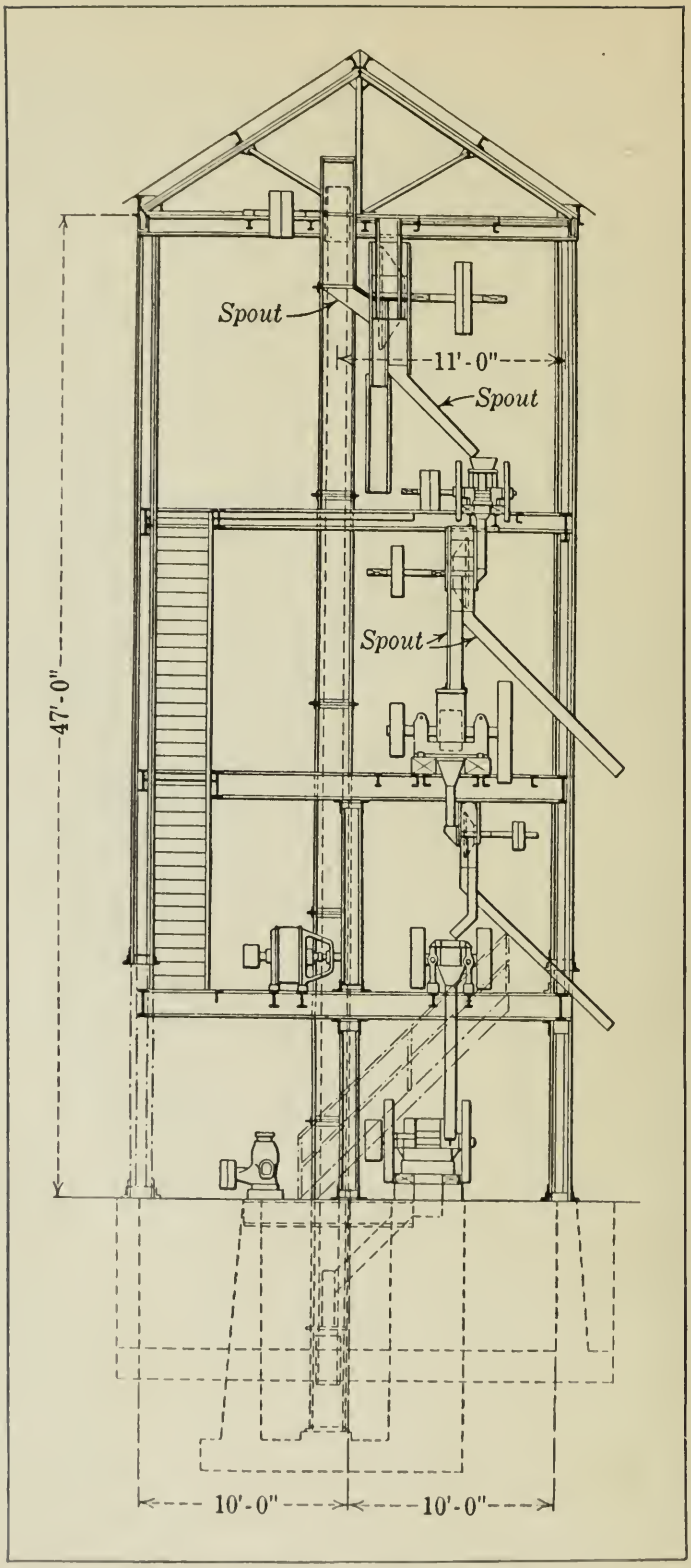

FIG. 247. A sampling plant

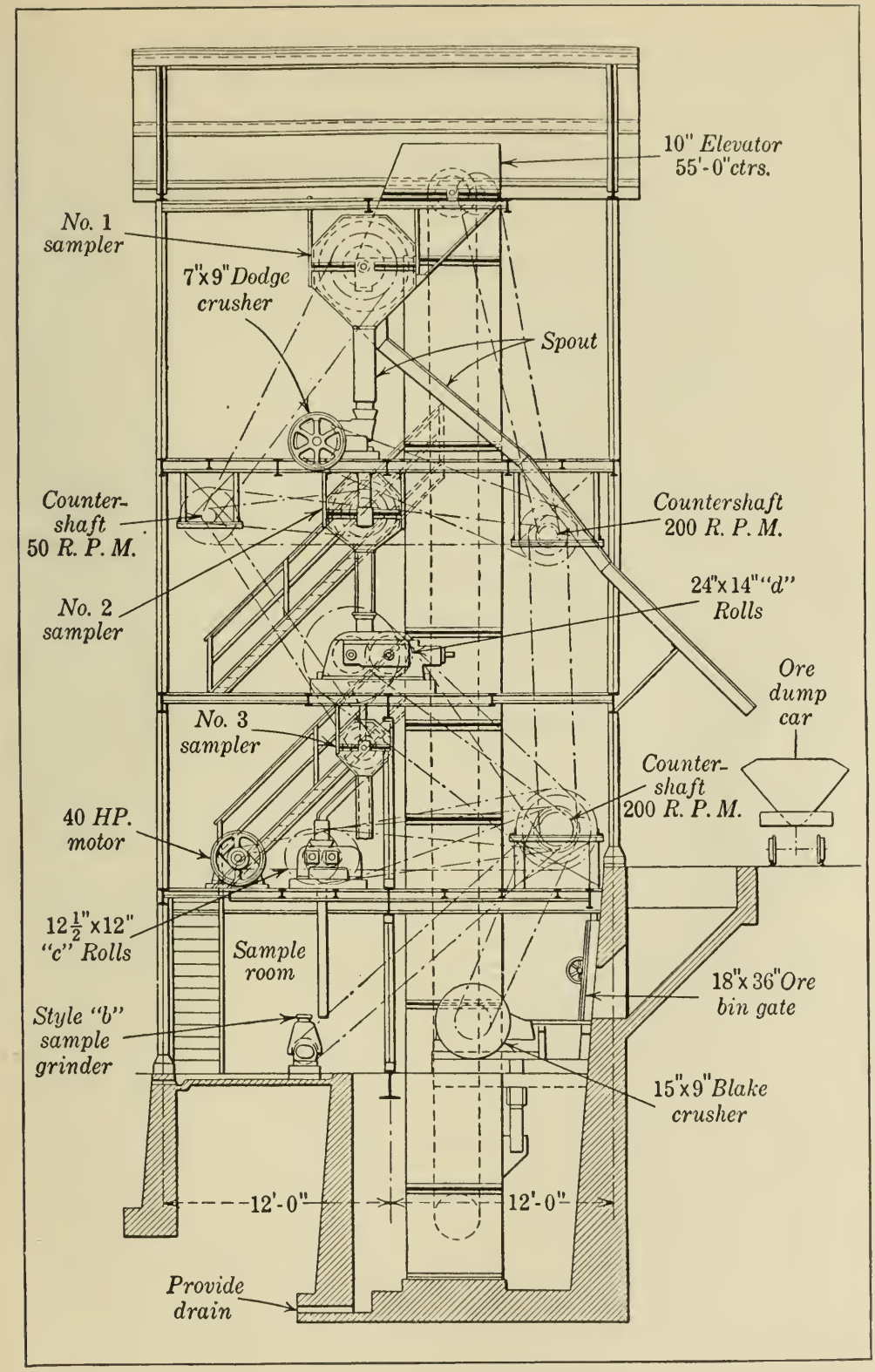

FIG. 248. A sampling plant

in the smelter contract, and if the umpire's results are within these allowances, the smelter assay stands. Settlement is made on that basis, and the shipper pays for the cost of the extra assay. If the original assay departs from these allowances, the smelter must stand the cost of the assay, and the settlement is corrected to correspond to them.

772. **Sampling base bullion.** Base bullion is impure lead from the blast furnace, containing from 50 to 500 ounces of Ag per ton. It usually contains a small amount of gold as well. Owing to the segregation of precious metals the exterior is richer than the interior, so that some care must be exercised in the sampling of such metal. For this purpose a punch is used, which, upon being driven into the bar, removes a piece of metal about $\frac{1}{8}$ inch in diameter and $1\frac{1}{2}$ inches long. Two chips are taken, one from the bottom and one from the top of each bar. The chips are taken at progressive distances from the end of the bar, the first 1 inch, the second $1\frac{1}{2}$ inches, the third 2 inches, and so on. This serves to equalize still further this segregation. From a carload of, say, 500 bars, chippings amounting to several pounds in weight would be taken. These are melted down in a graphite crucible to a quiet fusion and granulated by being poured into cold water, and a sample is picked for assay from these granules. Another and better way is to sample the lot as it is being cast into bars at the smelter.

773. **Sampling copper ingots.** A great deal of blister copper must be refined by electrolysis in order to recover the precious metals and rid the metal of certain impurities which detract from its mechanical strength or electrical conductivity. Electrolytic refining requires special and rather elaborate equipment, and costs too much if done on a small scale, so that most producers of raw copper prefer to send their product to a centrally located refinery. These are located at Baltimore, near New York City, and at Great Falls, Montana. Buyers of copper in large quantities must frequently sample their copper in order to see that it is of sufficient purity. The copper usually arrives in the shape of large ingots or slabs weighing from 100 to 700 pounds. In such shapes the segregation of precious metals and impurities is even more marked than in bars of base bullion. The following is an excellent method of sampling bars which have one large, flat face. A steel template is made,

of the same size as the face of the ingot. From 40 to 100 holes, depending upon the size, each about $\frac{1}{4}$ inch in diameter, are drilled in this template. These holes are evenly spaced over its surface and numbered in succession, starting at the upper left-hand corner of the template. The template is placed on the first bar to be sampled, a $\frac{3}{16}$-inch hole is drilled through the ingot in No. 1 hole, and the drillings are caught in a container. The second ingot is drilled through No. 2 hole, and so on until the entire lot has been sampled. From a carload of ingots several pounds of drillings will be collected, and if taken carefully they represent very accurately the shipment of metal.

MARKETING OF BULLION, ORES, AND CONCENTRATES

774. General. While, theoretically, every producer of a bullion, ore, or concentrate might erect a plant for the refining of the various contained metals, actually most producers are unable to do this, — first, because the erection of a smelter requires large and continued supplies of ore which the small producer is unable to obtain; second, because the large customs plant, in purchasing a great number of ores (calcareous, ferruginous, siliceous, etc.), often finds in one ore the fluxing constituent for another, while a small smelter, treating but one ore, might be obliged to bring worthless fluxing material long distances at an exorbitant cost.

Most of our metalliferous products are therefore treated at strategically located points throughout the country by what are known as customs smelters. Usually they reduce and refine but one or two metals, but in exceptional cases, five or six. For example, a smelter at El Paso might accept for treatment any kind of copper or lead ore; one at Danville, Illinois, any kind of zinc ore; a refinery at Perth Amboy, any kind of copper bullion; etc. While the customs smelter is ordinarily likened to an avaricious monster seeking to devour the poor, innocent producer, actually he is seeking to make a small profit under a rather difficult set of conditions. He must accept all kinds of material, wet and dry, fine and coarse, rich and poor, and sample this material accurately so that he will not pay the producer for more metal than the ore contains. He must then conduct his process, on such mixed materials, so as to recover,

in the presence of troublesome impurities, a high percentage of these metals. He must be able to anticipate market conditions and not become loaded up with unsalable metal or buy metal on a falling market. In short, the miner's troubles are usually ended when he has loaded the material into a railroad car, but the copper smelter's have just begun. He must face the risk of a considerable loss up to the moment when he markets his last pound of copper or ounce of silver.

775. Schedules. The buying and selling of metalliferous products is carried on by means of what is termed a schedule. This usually takes the form of a contract between the producer of the ore or bullion and the smelter or refinery. The seller agrees to furnish certain maximum and minimum amounts of ore over a specified period of months or years. This assures the smelter of a constant supply of material for his expensive plant. Then in this contract, which is often very complicated, are specified all the conditions of settlement, — just what percentage of the total metal will be paid for, the smelting charge, penalties for impurities and grades of ore lower than a certain standard, bonuses for higher grades of ore, and time and rate of payment. Since such settlement schedules vary between wide limits, it is perhaps best to take as examples a bullion, an ore, and a concentrate and show exactly how and on what basis settlement is made. Often, although individual items may vary considerably between two schedules, the net return to the shipper is much the same in both cases. The student must bear in mind that these are three actual settlements, and that practically all the charges, penalties, bonuses, etc. will vary from month to month and from company to company.

Lead Bullion

776. Treatment charge. The treatment charge is $16.25 per ton of material. If the silver content is in excess of 100 ounces per ton, the charge is to be increased at the rate of $1.00 per 100 ounces of excess.

777. Freight. The treatment charge is based on the present freight rate between refining plant and smelter, any increase or decrease to be adjusted in settlement. The bullion must be

delivered on cars at the refining plant, the buyer paying for unloading and other incidental expenses.

778. Gold. If the gold content is in excess of 0.05 ounce per ton, the refiner pays for it at the rate of $19.02 per ton.

779. Silver. The refiner pays 99 per cent of the price quoted on the thirtieth day after arrival at the refining plant, less a refining charge of $0.01 per ounce when silver is quoted above $0.65 per ounce. The price of silver used is the Handy and Harman quotation in the *Engineering and Mining Journal.*

780. Lead. The refiner pays for 99 per cent of the lead at the average price of lead for the fifteen days after arrival, less a selling commission.

781. Impurities. Any excess over 1.5 per cent of As, Sb, and Bi combined is to be penalized as follows: 1.5 to 3 per cent of As, Sb, and Bi, at $1.00 per unit per ton; all above 3 per cent of As, Sb, and Bi, at $1.50 per unit per ton.

782. Payment. The refiner will pay for the silver value, less charges, thirty days after the arrival of the shipment at the refinery; for the lead value, less charges, forty-five days after the arrival of the shipment at the refinery.

783. Splitting limits. If the analysis of the buyer and that of the seller agree within the "splitting limits," the arithmetical average is taken as a basis of settlement. These limits are

Ag	0.60 ounce per ton
Au	0.035 ounce per ton
Pb	0.40 per cent
As + Sb + Bi	0.30 per cent

Let us now consider the settlement of a shipment of two cars of bullion, containing 1695 bars of the following composition:

Pb	95.075 per cent
Ag	108.80 ounces per ton
Au	0.6655 ounce per ton
As	1.01 per cent
Sb	2.55 per cent
Bi	0.02 per cent
Moisture	None

An actual settlement according to the schedule of one of our large metallurgical concerns is given in tabulated form in Table LXXXIV on the following page.

TABLE LXXXIV. SETTLEMENT OF SHIPMENT OF LEAD BULLION

Net weight of 1695 bars = 158,396 lb. = 79.198 tons

Net contents			
Au, 52.706 oz.			
Ag, 8616.74 oz.			
Pb, 150,595 lb.			
Value of contents			
Au, 52.706 oz. @ $19.02			$1002.47
Ag, 99% of 8616.74 oz. @ $0.55979			4775.33
Pb, 99% of 150,595 lb. @ $0.04856057			8730.99
Total value			$14,508.79
Penalties			
1.50% As, Sb, Bi @ $1.00 = $1.50			
0.58% As, Sb, Bi @ $1.50 = 0.87			
	$2.37		
Treatment charge			
Base	$16.25		
Excess silver	0.088		
Freight differential	2.56963		
Penalties	2.37		
	$21.27763		
Total charge			
Treatment @ $21.27763		$1685.15	
Umpire assay		15.00	
Total		$1700.15	1700.15
Net to shipper			$12,808.64

COPPER ORE

784. Weighing, sampling, and representation. All weighing and sampling must be done at the refining works in the presence of the shipper's representative. All expenses of these operations will be charged to the shipper's account.

785. Gold. If the ore contains less than 0.03 ounce of Au per ton, there will be no payment. If it contains more than 0.03 ounce per ton, all the gold will be paid for at the rate of $20 per ounce.

786. Silver. Payment will be made for 95 per cent of the silver contents at the official New York quotation, with a minimum deduction of 1 ounce per ton.

787. Copper. Copper must be determined by the electrolytic method. If wet assay is used, deduct 1.3 units. All the copper to be paid for at the official New York quotation.

788. Smelting charge. Base charge to be $3.00 per ton of 2000 pounds.

789. Refining charge. To be $0.02 per pound of copper.

790. Penalties. As, Sb, and Bi to be combined. All in excess of 1 per cent to be penalized at the rate of $1.00 per unit per ton. Fractions pro rata.

791. Payment. Payment to be made seventy-five days after the arrival of the shipment at the refinery.

792. Quotations. The average quotation of the *Engineering and Mining Journal* for the calendar week following the week of the arrival of the material at the refinery.

Let us now consider the settlement of the following ore:

Moisture	1.28 per cent
Cu	23.85 per cent
Au	0.05 ounce per ton
Ag	48.125 ounces per ton
As	0.37 per cent
Sb	0.15 per cent
Bi	Trace

This settlement is tabulated in Table LXXXV.

TABLE LXXXV. SETTLEMENT OF SHIPMENT OF COPPER ORE

166,415 lb. @ 1.28% H_2O = 164,285 lb. dry, or 82.1425 tons

Net contents		
Au, 4.107 oz.		
Ag, 3953.11 oz.		
Cu, 37,046 lb.		
Value of contents		
Au, 4.107 oz. @ $20 per ounce		$82.14
Ag, 95% of 3953.11 oz. @ $0.552083		2073.32
Cu, 37,046 lb. @ $0.130458		4832.95
		$6988.41
Penalties		
As, Sb, plus Bi, less than 1 per cent; so no deduction.		
Total charge		
Treatment of 82.1425 tons @ $3.00	$246.43	
Refining of 37,046 lb. @ $0.02	740.92	
Lighterage of 82.1425 tons @ $1.00	82.14	
Umpire assay	4.00	
Total	$1073.49	1073.49
Net to shipper		$5914.92

ZINC CONCENTRATE

793. Zinc. The smelter will pay for 75 per cent of the zinc content at the average price (as quoted in the *Engineering and Mining Journal*) for ordinary Prime Western brand of slab zinc, for the week covering the date of arrival of the ore at the plant.

794. Lead. The smelter will pay for 80 per cent of the lead content at the average price (as quoted in the *Engineering and Mining Journal*) for the calendar week following the week of arrival at the smelter, less \$0.0165 per pound.

795. Silver. The smelter will pay for 80 per cent of silver content at the Handy and Harman quotation as given in the *Engineering and Mining Journal* on the date of final settlement.

796. Treatment charge. The nominal treatment charge is \$19.50 when the St. Louis quotation for slab zinc (as given in the *Engineering and Mining Journal*) is 4 cents per pound. Each cent or fractional part of a cent above this base is charged for at the rate of \$3.00 per unit.

Let us now examine a smelter settlement (shown in Table LXXXVI) for a zinc concentrate of the following composition:

Zn	43.6 per cent
Pb	5.0 per cent
Cu	0.4 per cent
Insol.	7.7 per cent
Fe	9.0 per cent
CaO	1.5 per cent
S	27.7 per cent
Ag	7.4 ounces per ton

TABLE LXXXVI. SETTLEMENT OF SHIPMENT OF ZINC CONCENTRATES

86,420 lb. @ 2.5% H_2O = 83,284 lb. = 41.642 tons

Net contents		
Zn, 36,312 lb.		
Pb, 4164 lb.		
Ag, 293.2 oz.		
Value of contents		
Zn, 75% of 36,312 lb. @ \$0.07125		\$1940.42
Pb, 80% of 4164 lb. @ (\$0.0665 − \$0.0165)		166.56
Ag, 80% of 293.2 oz. @ \$0.653 per ounce		153.17
		\$2260.15
Total charge		
Treatment, \$19.50 + (7.125 − 4) @ \$3.00	\$1202.20	
Freight, 41.642 @ \$7.50	312.32	
Total	\$1514.52	1514.52
Net to shipper		\$745.63

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